

* NOTICES *

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2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] (a) The positive type chemistry magnification resist constituent characterized by containing the compound which generates a radical (A) directly or indirectly by the exposure of an energy line.

[Claim 2] (b) The positive type chemistry magnification resist constituent according to claim 1 characterized by containing the compound which generates an acid by the exposure of an energy line.

[Claim 3] (c) The positive type chemistry magnification resist constituent according to claim 1 or 2 characterized by having the radical which may be decomposed with an acid, and the solubility over an alkali developer being insoluble in the resin which increases according to an operation of an acid, or (g) water, and containing meltable resin in an alkali developer.

[Claim 4] (f) The positive type chemistry magnification resist constituent according to claim 1 to 3 characterized by containing the with a molecular weight of 3000 or less low-molecular lysis inhibition compound to which it has the radical which may be decomposed with an acid and the solubility over an alkali developer increases according to an operation of an acid.

[Claim 5] The positive type chemistry magnification resist constituent according to claim 1 to 4 characterized by for this radical (A) reacting with the compound (a) which generates an acid by the exposure of the (a) energy line, and generating an acid.

[Claim 6] The positive type chemistry magnification resist constituent according to claim 1 to 5 characterized by the thing for which this compound (a) is chosen from the following group, and which is a kind at least.

** Alkyl halides other than a fluorine, aryl halides other than a fluorine, Halogenation aralkyls other than a fluorine, allyl halides other than a fluorine (However, as for the above-mentioned alkyl, aryl, an aralkyl, and an allyl group, a part or all hydrogen may be permuted by the fluorine) ** Thiol compounds, the second class alcohol, the allyl alcohol that may have a substituent, The shape of a benzyl alcohol [which may have a substituent on a ring] and these ester, ether compound sulfide compound, disulfide compound ** halogen-containing silicon compound, and alkoxy silicon compound ** straight chain, the letter of branching, or an annular acetal compound **N-hydroxyl compound

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the positive type chemistry magnification resist constituent which was excellent in the pattern profile exposed and obtained through an electron ray or an X-ray about the positive type chemistry magnification resist constituent, was excellent in resolving power, lengthened further, placed by high sensitivity, and was excellent in stability (PCD, PED) with the passage of time. PCD (Post Coating Delay) stability is the paint film stability at the time of leaving it within [after applying a resist constituent to a substrate] irradiation equipment, and out of equipment, and PED (Post Exposure Delay) stability is the paint film stability at the time of leaving it within irradiation equipment and out of equipment here until it performs heating actuation after an exposure.

[0002]

[Description of the Prior Art] the integrated circuit is raising the degree of integration increasingly, and consists of the line breadth of a HAFUMIN cron less or equal in manufacture of semi-conductor substrates, such as a VLSI, -- processing of a detailed pattern has overly come to be needed. Therefore, the chemistry magnification resist is used as a resist ingredient for lithography.

[0003] Especially as for an electron ray or an X-ray, the next generation or development of the positive-resist constituent which is positioned as a generation's pattern formation technique one after another, and can attain high sensitivity, high resolution, and a rectangle profile configuration is desired.

[0004] Furthermore, in the case of a positive type chemistry magnification resist, that it is [which is put the effect of the basic pollutant in atmospheric air, or within and without irradiation equipment] easy to be influenced (desiccation of a paint film), the front face made it refractory, and when it was the Rhine pattern, it became a T-Top configuration (a front face becomes T character-like eaves), and in the case of a contact hole pattern, there was a problem that a front face became a capping configuration (it is eaves formation to a contact hole front face). Furthermore, it got worse also about the stability (PCD, PED) in the passage of time in irradiation equipment and besides equipment, and the problem of changing a pattern dimension was also produced.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the positive type chemistry magnification resist constituent which has high sensitivity and high resolution, could give the pattern profile which was excellent in the shape of a rectangle, and was moreover excellent in PCD and PED stability. Other purposes of this invention are to offer the positive type chemistry magnification resist constituent excellent in spreading nature (homogeneity within a field).

[0006]

[Means for Solving the Problem] That is, according to this invention, the following positive type chemistry magnification resist constituent is offered, and the above-mentioned purpose of this invention is attained.

[0007] (1) The positive type chemistry magnification resist constituent characterized by containing the compound which generates a radical (A) directly or indirectly by the exposure of the (a) energy line.

[0008] (2) A positive type chemistry magnification resist constituent given in the above (1) characterized by containing the compound which generates an acid by the exposure of the (b) energy line.

[0009] (3) The above (1) characterized by having the radical which may be decomposed with the (e) acid, and the solubility over an alkali developer being insoluble in the resin which increases according to an operation of an acid, or

(g) water, and containing meltable resin in an alkali developer, or a positive type chemistry magnification resist constituent given in (2).

[0010] (4) A positive type chemistry magnification resist constituent given in either of aforementioned (1) - (3) characterized by containing the with a molecular weight of 3000 or less low-molecular lysis inhibition compound to which it has the radical which may be decomposed with the (f) acid, and the solubility over an alkali developer increases according to an operation of an acid.

[0011] (5) A positive type chemistry magnification resist constituent given in either of aforementioned (1) - (4) characterized by for this radical (A) reacting with the compound (a) which generates an acid by the exposure of the (a) energy line, and generating an acid.

[0012] (6) A positive type chemistry magnification resist constituent given in either of aforementioned (1) - (5) characterized by the thing for which this compound (a) is chosen from the following group, and which is a kind at least.

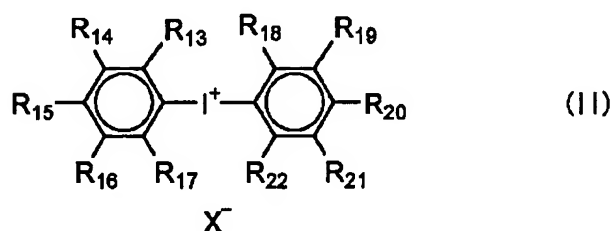
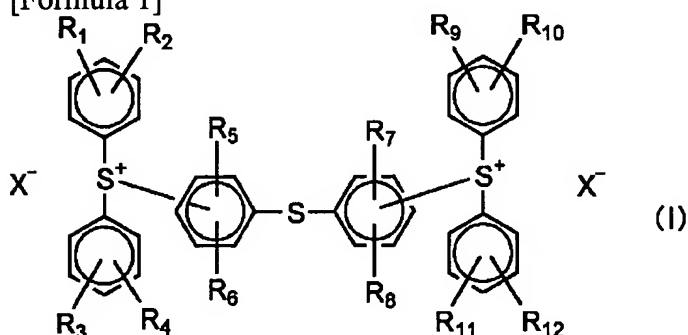
** Alkyl halides other than a fluorine, aryl halides other than a fluorine, Halogenation aralkyls other than a fluorine, allyl halides other than a fluorine (However, as for the above-mentioned alkyl, aryl, an aralkyl, and an allyl group, a part or all hydrogen may be permuted by the fluorine) ** Thiol compounds, the second class alcohol, the allyl alcohol that may have a substituent, The benzyl alcohol which may have a substituent on a ring, and these ester, The shape of an ether compound sulfide compound, disulfide compound ** halogen-containing silicon compound, and alkoxy silicon compound ** straight chain, the letter of branching, or an annular acetal compound **N-hydroxyl compound

[0013] A desirable mode is indicated below.

(7) A positive type chemistry magnification resist constituent given in either of aforementioned (1) - (6) characterized by this compound (b) containing at least one of the compounds expressed with the following general formula (I) - (II).

[0014]

[Formula 1]



[0015] the inside of a formula, and R1-R22 are the same -- or it differs and the shape of the shape of a hydrogen atom and a straight chain, the letter of branching or an annular alkyl group, and a straight chain, the letter of branching or an annular alkoxy group, hydroxyl, a halogen atom, or 23 -S-R are expressed. R23 expresses the shape of a straight chain, the letter of branching, an annular alkyl group, or an aryl group. Moreover, two or more of R1-R12, and R13-R22 may join together, and the ring containing one sort chosen from single bond, carbon, oxygen, sulfur, and nitrogen or two sorts or more may be formed. X- is the anion of a sulfonic acid.

[0016] (8) The shape of a straight chain by which X- was permuted by at least one fluorine atom and at least one fluorine atom, The shape of a straight chain permuted by the letter of branching or the annular alkyl group, and at least one fluorine atom, The acyl group permuted by the letter of branching or the annular alkoxy group, and at least one

fluorine atom, The acyloxy radical permuted by at least one fluorine atom, the sulfonyl group permuted by at least one fluorine atom, The sulfonyloxy radical permuted by at least one fluorine atom, the sulfonylamino radical permuted by at least one fluorine atom, The aryl group permuted by at least one fluorine atom, the aralkyl radical permuted by at least one fluorine atom, And the alkoxy carbonyl group permuted by at least one fluorine atom, since -- a positive type chemistry magnification resist constituent given in the above (7) characterized by being the anion of the alkyl sulfonic acid which has at least one selected sort, benzenesulfonic acid, a naphthalene sulfonic acid, or an anthracene sulfonic acid.

[0017] (9) A positive type chemistry magnification resist constituent given in either of aforementioned (1) - (8) characterized by containing (c) organic base nature compound further.

(10) A positive type chemistry magnification resist constituent given in either of aforementioned (1) - (9) characterized by containing further (d) fluorine system and/or a silicon system surface active agent.

[0018] (11) A positive type chemistry magnification resist constituent given in either of aforementioned (1) - (10) characterized by mainly including propylene-glycol-monomethyl-ether acetate as a solvent.

(12) A positive type chemistry magnification resist constituent given in either of aforementioned (1) - (11) characterized by an energy line being an electron ray or an X-ray.

[0019]

[Embodiment of the Invention] Hereafter, the positive type chemistry magnification resist constituent of this invention is explained.

The compound which generates a radical (A) directly or indirectly by the exposure of the [I (a)] energy line (it is also called the (a) component or the compound of (a))

In addition, the above-mentioned energy line expresses the light, ultraviolet rays, an electron ray, or an X-ray.

[0020] It means generating a radical at the reaction in which only one molecule participates [this compound molecule] generating a radical directly by the exposure of an electron ray or an X-ray, and means that this compound molecule generates a radical at the reaction in which other molecules or other compound molecules of this compound, and more than dyad participate generating a radical indirectly.

[0021] Although any compound can be used if it is the compound which fulfills the above-mentioned conditions as a compound of (a) used for this invention, the thing which is chosen from the following group and which is a kind at least is desirable.

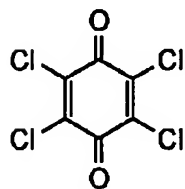
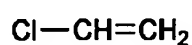
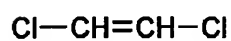
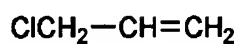
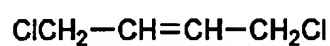
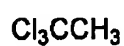
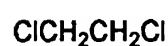
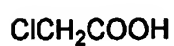
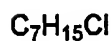
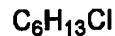
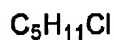
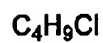
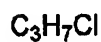
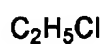
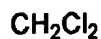
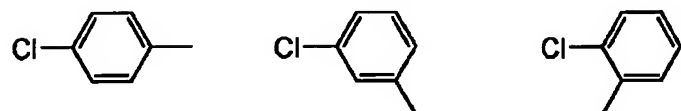
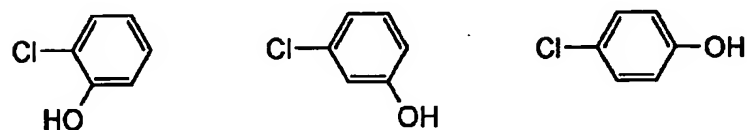
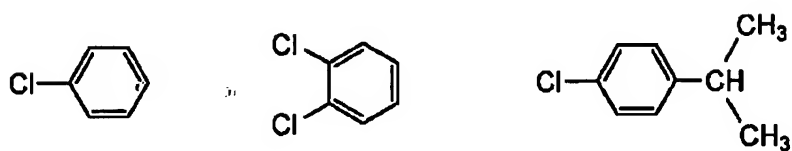
[0022] ** Alkyl halides other than a fluorine, aryl halides other than a fluorine, Halogenation aralkyls other than a fluorine, allyl halides other than a fluorine (However, as for the above-mentioned alkyl, aryl, an aralkyl, and an allyl group, a part or all hydrogen may be permuted by the fluorine) ** Thiol compounds, the second class alcohol, the allyl alcohol that may have a substituent, The benzyl alcohol which may have a substituent on a ring, and these ester, The shape of an ether compound sulfide compound, disulfide compound ** halogen-containing silicon compound, and alkoxy silicon compound ** straight chain, the letter of branching, or an annular acetal compound **N-hydroxyl compound [0023] The compound of the above-mentioned ** - ** is explained one by one below.

[0024] ** As for the above-mentioned alkyl, aryl, the aralkyl, and the allyl group, a part or all hydrogen atoms may be permuted by the fluorine atom among the compound of ** about the compound, and the above-mentioned alkyl and an aralkyl substituent may branch further.

[0025] Although the example of these compounds is given to below, it is not limited to these.

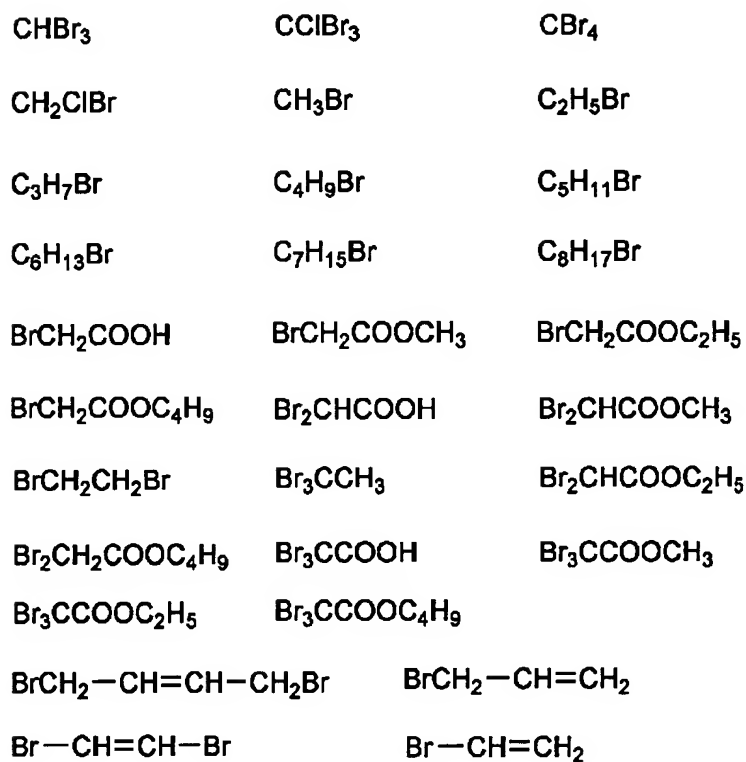
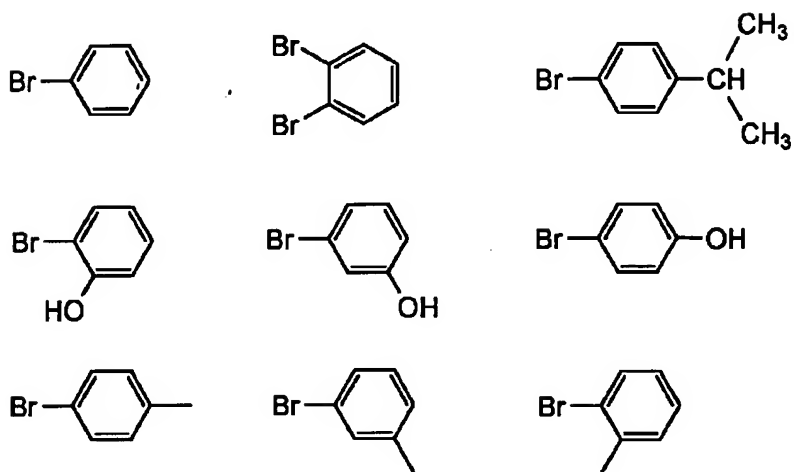
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[Formula 2]

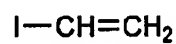
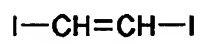
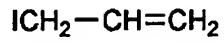
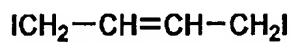
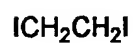
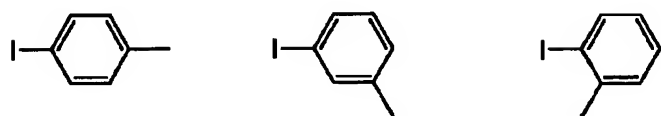
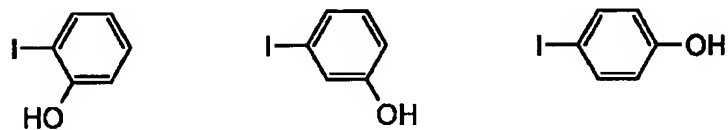
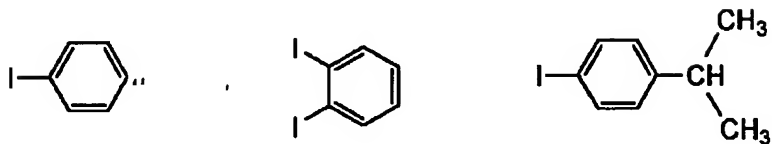


[0027]

[Formula 3]

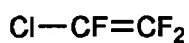
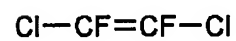
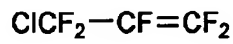
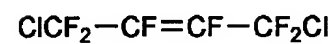
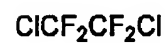
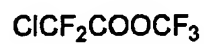
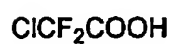
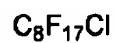
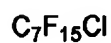
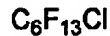
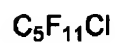
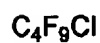
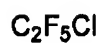
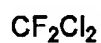
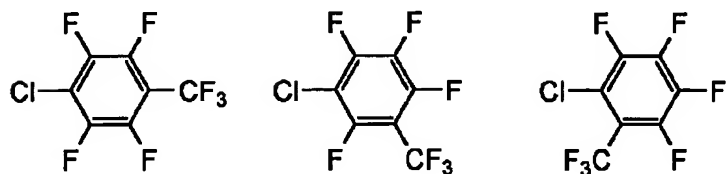
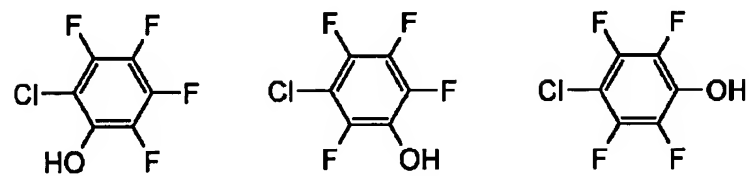
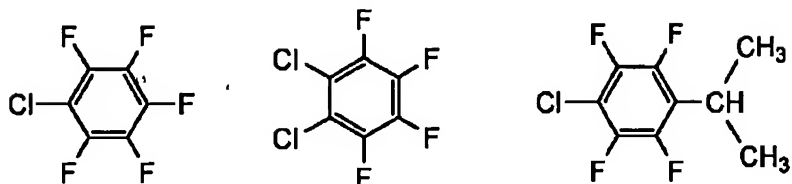


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[Formula 4]



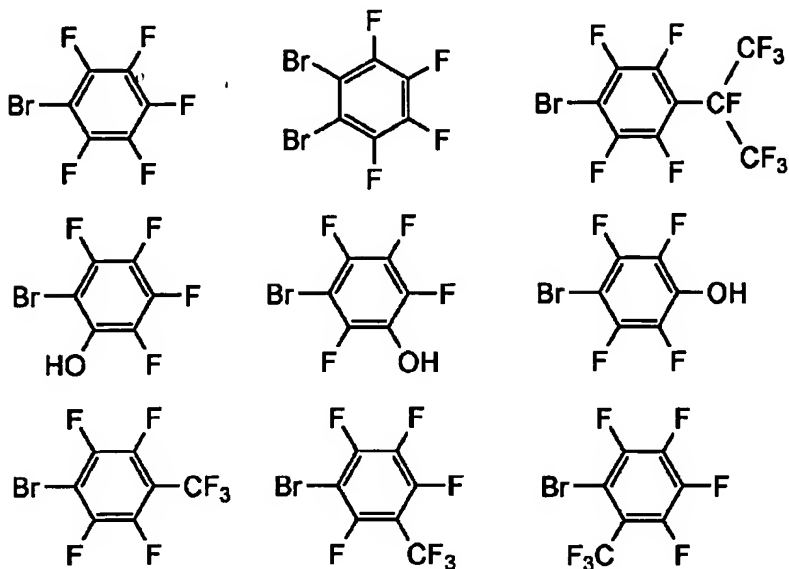
[0029]

[Formula 5]



[0030]

[Formula 6]



CFBr_3

CF_2ClBr

CF_3Br

$\text{C}_2\text{F}_5\text{Br}$

$\text{C}_3\text{F}_7\text{Br}$

$\text{C}_4\text{F}_9\text{Br}$

$\text{C}_5\text{F}_{11}\text{Br}$

$\text{C}_6\text{F}_{13}\text{Br}$

$\text{C}_7\text{F}_{15}\text{Br}$

$\text{C}_8\text{F}_{17}\text{Br}$

BrCF_2COOH

$\text{BrCF}_2\text{COOCF}_3$

$\text{BrCF}_2\text{COOC}_2\text{F}_5$

$\text{BrCF}_2\text{COOC}_4\text{F}_9$

Br_2CFCOOH

$\text{Br}_2\text{CFCOOCF}_3$

$\text{BrCF}_2\text{CF}_2\text{Br}$

Br_3CCF_3

$\text{Br}_2\text{CFCOOC}_2\text{F}_5$

$\text{Br}_2\text{CF}_2\text{COOC}_4\text{F}_9$

Br_3CCOOH

$\text{Br}_3\text{CCOOCF}_3$

$\text{Br}_3\text{CCOOC}_2\text{F}_5$

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$\text{BrCF}_2-\text{CF}=\text{CF}-\text{CF}_2\text{Br}$

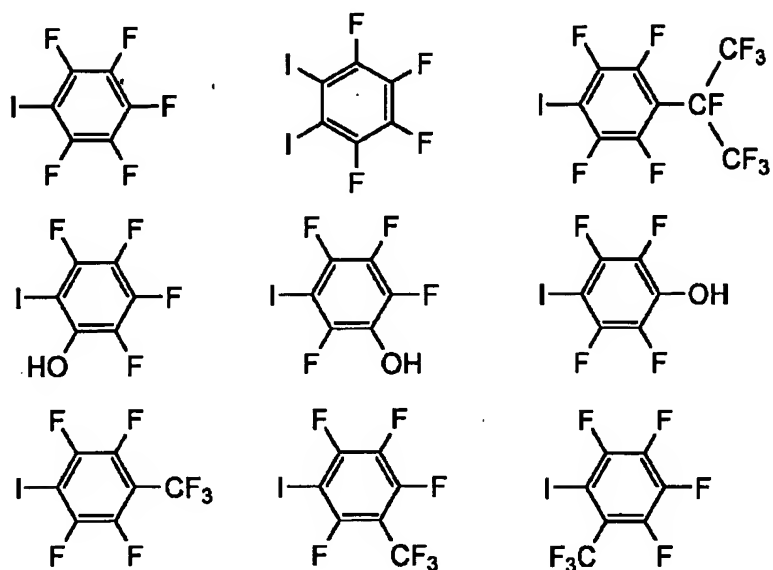
$\text{BrCF}_2-\text{CF}=\text{CF}_2$

$\text{Br}-\text{CF}=\text{CF}-\text{Br}$

$\text{Br}-\text{CF}=\text{CF}_2$

[0031]

[Formula 7]

CFI₃CF₂CICF₃IC₂F₅IC₃F₇IC₄F₉IC₅F₁₁IC₆F₁₃IC₇F₁₅IC₈F₁₇IICF₂COOHICF₂COOCF₃ICF₂COOC₂F₅ICF₂COOC₄F₉I₂CF₂COOHI₂CF₂COOCF₃ICF₂CF₂II₃CCF₃I₂CF₂COOC₂F₅I₂CF₂COOC₄F₉I₃CCOOHI₃CCOOCF₃I₃CCOOC₂F₅I₃CCOOC₄F₉ICF₂—CF=CF—CF₂IICF₂—CF=CF₂

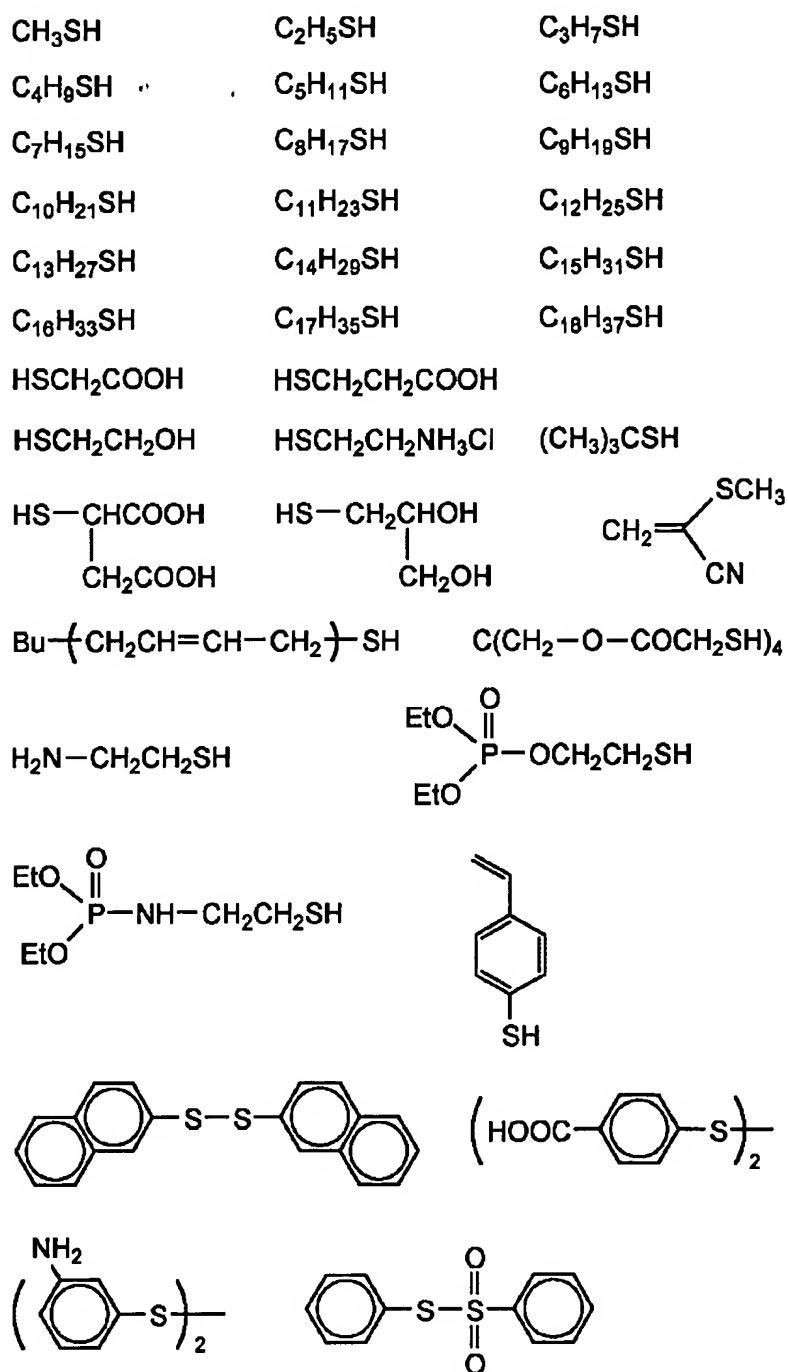
I—CF=CF—I

I—CF=CF₂

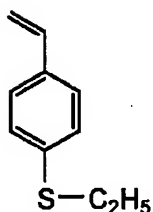
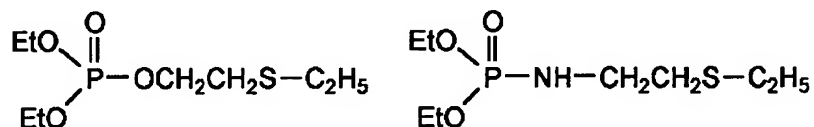
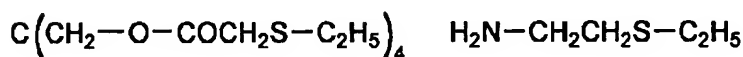
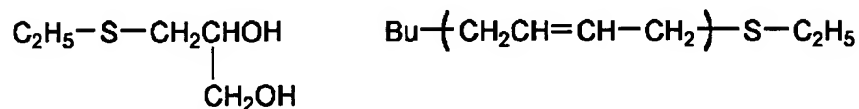
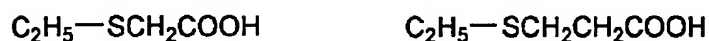
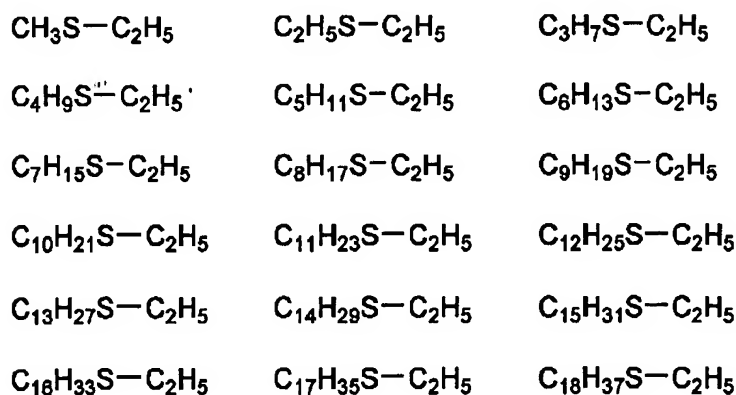
[0032] ** Although the example of these compounds is given to below about a compound, it is not limited to these.

[0033]

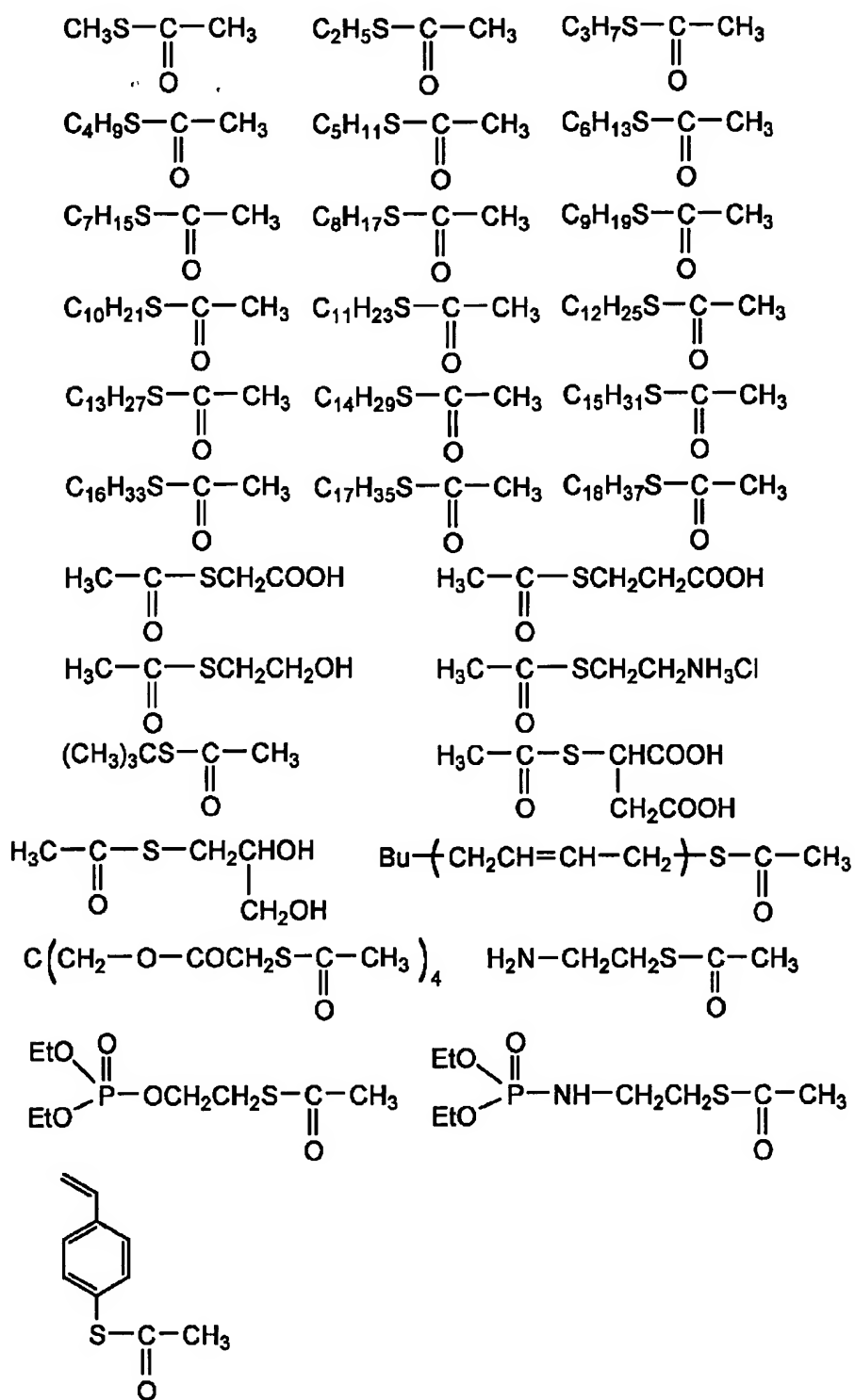
[Formula 8]



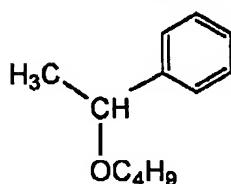
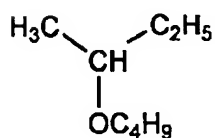
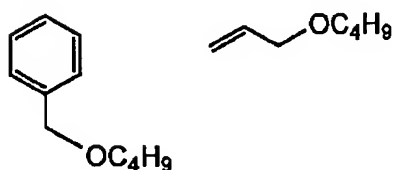
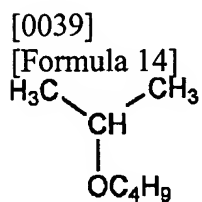
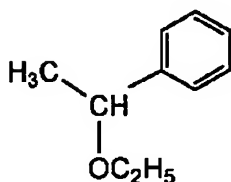
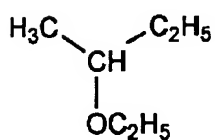
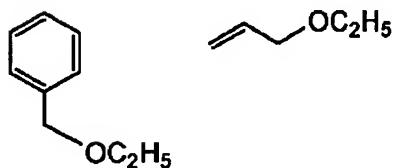
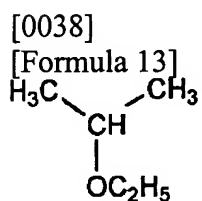
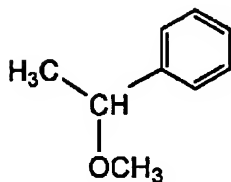
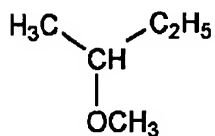
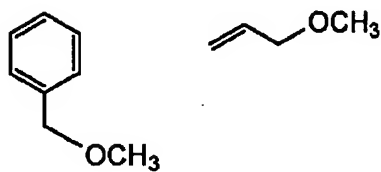
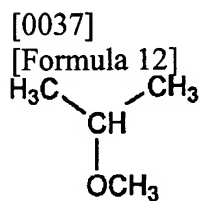
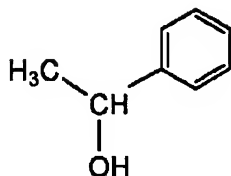
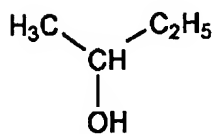
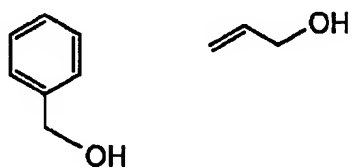
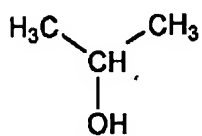
[0034]
[Formula 9]



[0035]
[Formula 10]

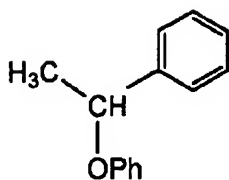
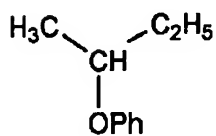
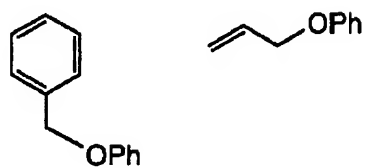
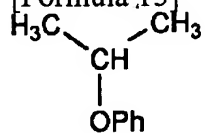


[0036]
[Formula 11]



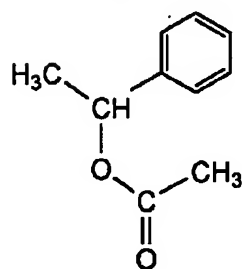
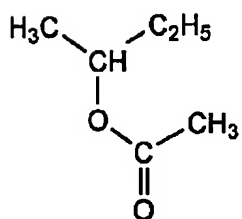
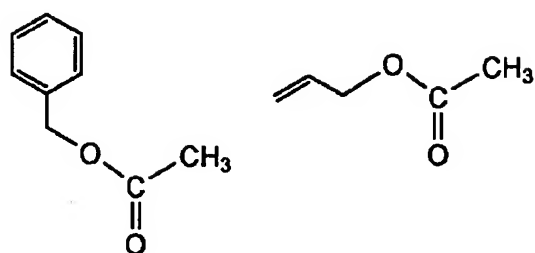
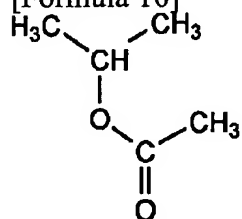
[0040]

[Formula 15]



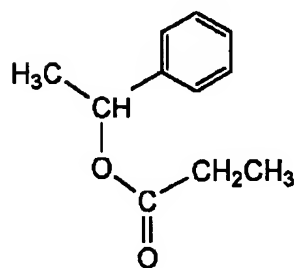
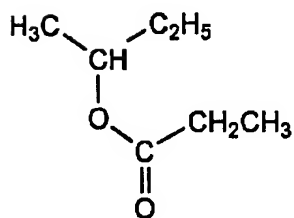
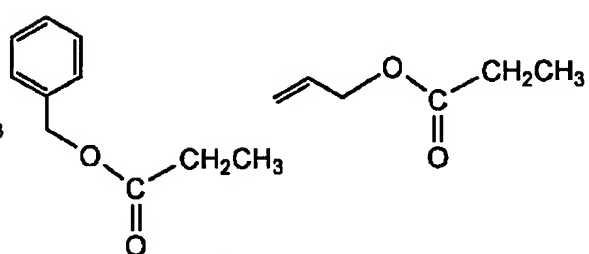
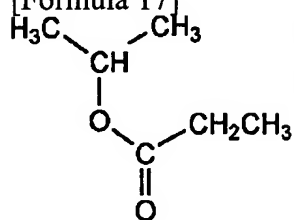
[0041]

[Formula 16]



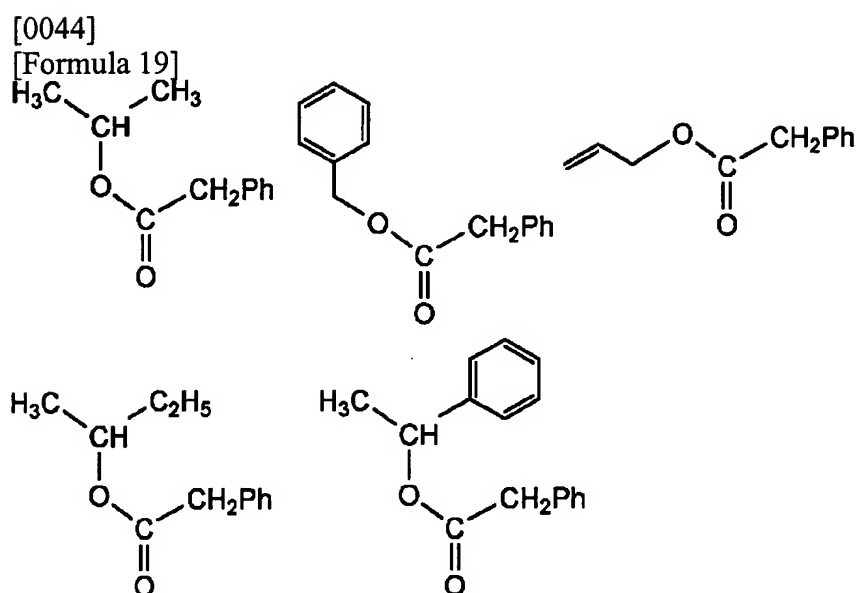
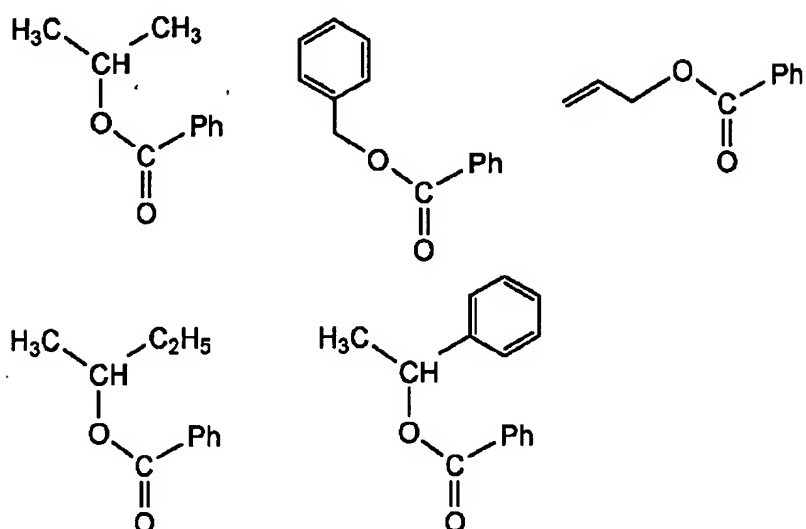
[0042]

[Formula 17]



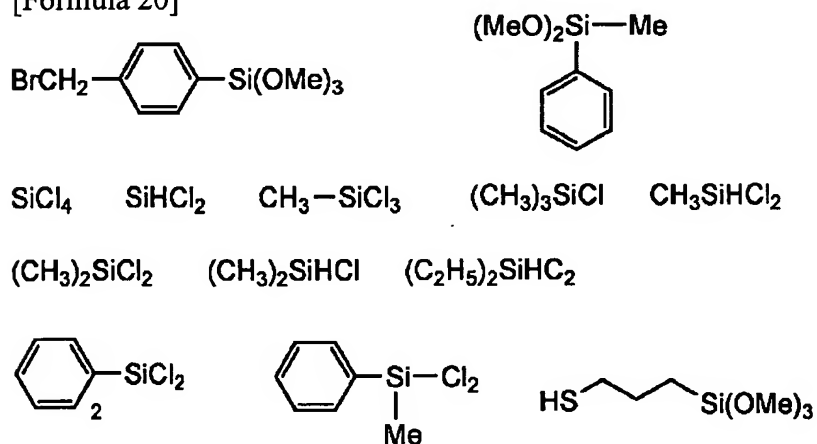
[0043]

[Formula 18]



[0045] ** Although the example of these compounds is given to below about a compound, it is not limited to these.

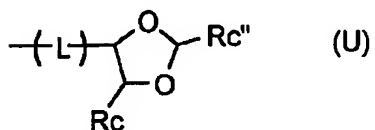
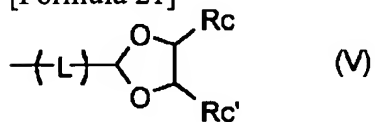
[0046]
[Formula 20]



[0047] ** As these compounds, the compound which has the substructure expressed with the following general formula (V) and (U) is desirable about a compound.

[0048]

[Formula 21]



[0049] R_c, R_{c'}, R_{c''}; you may differ, and the same, the alkyl group which may have the hydrogen atom and the substituent, or an aryl group may be expressed, and two of them may join together, and the ring of saturation or olefin nature partial saturation may be formed. L expresses a divalent connection radical.

[0050] In a general formula (V) and (U), R_c, R_{c'}, and when R_{c''} is an aryl group, generally it has 4-20 carbon atoms, and an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an acyl group, an acyloxy radical, an alkyl sulfhydryl group, an aminoacyl radical, a carboalkoxy radical, the nitro group, the sulfonyl group, the cyano group, or the halogen atom may permute. Here, as an aryl group of 4-20 carbon numbers, a phenyl group, a tolyl group, a xylyl group, a biphenyl radical, a naphthyl group, an anthryl radical, a phenan tolyl group, etc. are mentioned, for example.

[0051] R_c, R_{c'}, and when R_{c''} expresses an alkyl group, the alkyl group of the straight chain of the saturation of carbon numbers 1-20 or partial saturation, branching, or alicycle is shown, and a halogen atom, a cyano group, an ester group, the oxy-radical, the alkoxy group, the aryloxy group, or the aryl group may permute. Here as an alkyl group of the straight chain of the saturation of 1-20 carbon numbers, or partial saturation, branching, or alicycle A methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, t-butyl, a pentyl radical, an isopentyl radical, a neopentyl radical, a hexyl group, An iso hexyl group, an octyl radical, an iso octyl radical, a nonyl radical, a decyl group, An undecyl radical, the dodecyl, a tridecyl radical, a tetradecyl radical, a vinyl group, A propenyl radical, a butenyl group, 2-butenyl group, 3-butenyl group, an iso butenyl group, A pentenyl radical, 2-pentenyl radical, a hexenyl radical, a heptenyl radical, an octenyl group, A cyclo propyl group, cyclo butyl, a cyclopentylic group, a cyclohexyl radical, a cycloheptyl radical, a cyclo octyl radical, a cyclo pentenyl radical, a cyclohexenyl group, etc. can be illustrated.

[0052] moreover, R_c, R_{c'}, and R_{c''} -- the ring of the saturation which any two of 'combine and form, or olefin nature partial saturation -- concrete -- as cycloalkane or cycloalkene -- usually -- 3-8 -- 5 or six ring members are expressed preferably. As a divalent connection radical of L, the alkylene group and cyclo alkylene group which may have single bond and a substituent, an arylene radical or -O-, -O-CO-Ra1-, -CO-O-Ra2-, and -CO-N(Ra3)-Ra4- are expressed. Ra1, Ra2, and Ra4 express the same alkylene group which may differ but, may have single bond or ether structure, ester structure, amide structure, urethane structure, or ureido structure, and may have the substituent, a cyclo alkylene group, and an arylene radical. Ra3 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, and an aryl group.

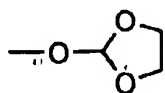
[0053] In this invention, R_c, R_{c'}, and the thing whose R_{c''} is a hydrogen atom or the alkyl group of 1-4 carbon numbers are desirable in a general formula (V) and (U).

[0054] Although the example of a compound of having the substructure expressed with a general formula (V) and (U) below is given, it is not limited to these.

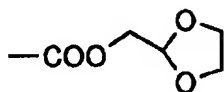
[0055]

[Formula 22]

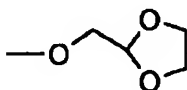
(V-1)



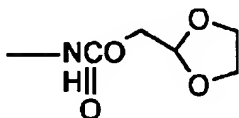
(V-2)



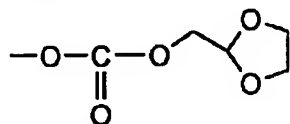
(V-3)



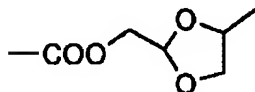
(V-4)



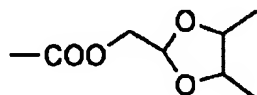
(V-5)



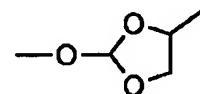
(V-6)



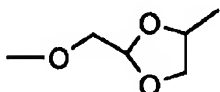
(V-7)



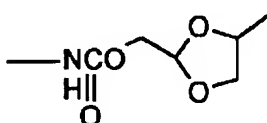
(V-8)



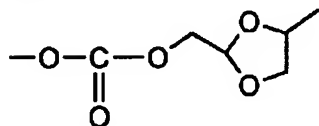
(V-9)



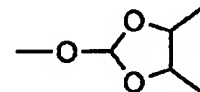
(V-10)



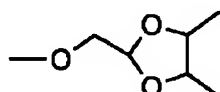
(V-11)



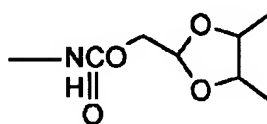
(V-12)



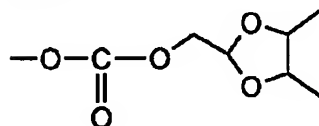
(V-13)



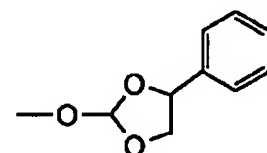
(V-14)



(V-15)



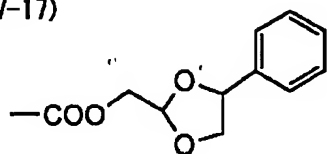
(V-16)



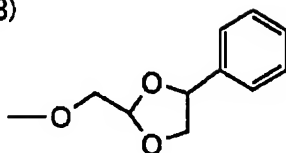
[0056]

[Formula 23]

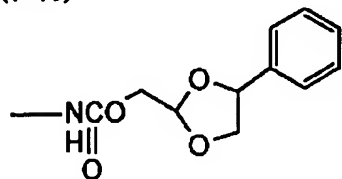
(V-17)



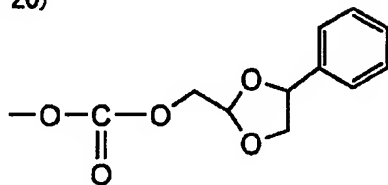
(V-18)



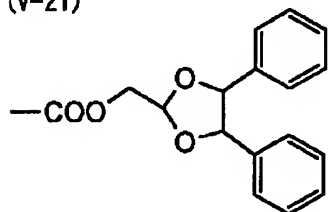
(V-19)



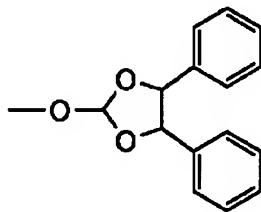
(V-20)



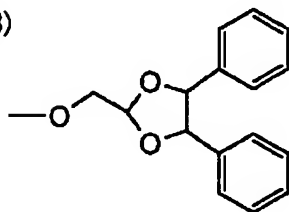
(V-21)



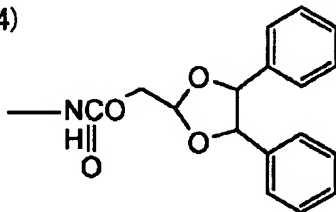
(V-22)



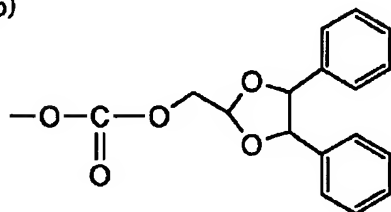
(V-23)



(V-24)

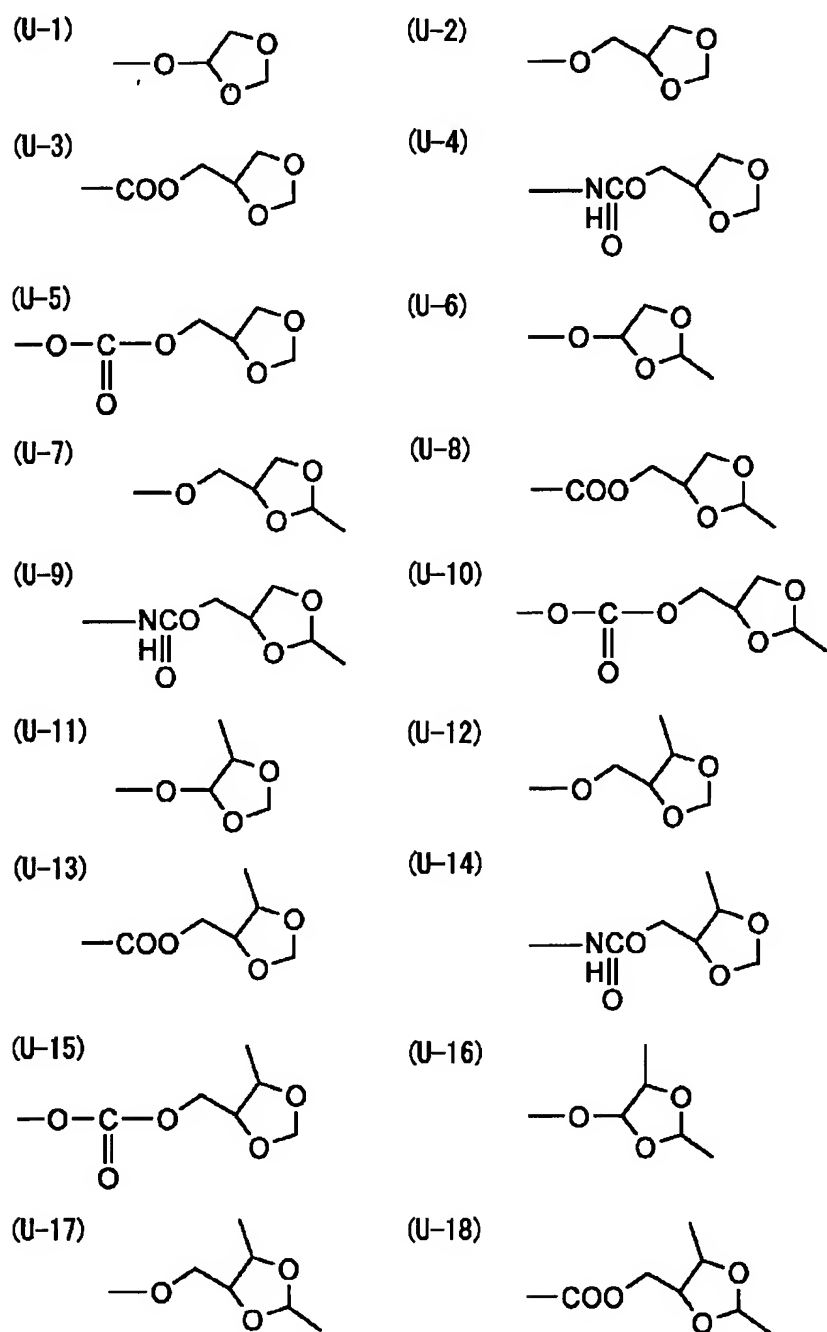


(V-25)



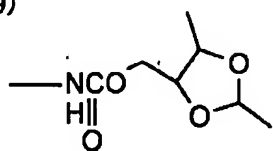
[0057]

[Formula 24]

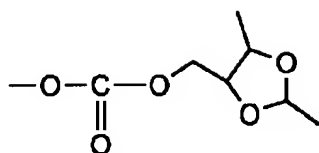


[0058]
[Formula 25]

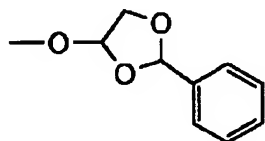
(U-19)



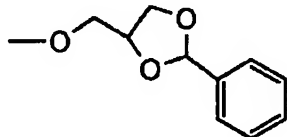
(U-20)



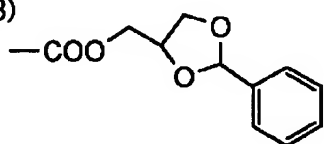
(U-21)



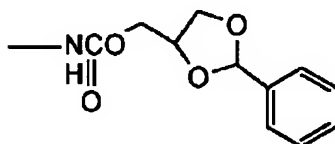
(U-22)



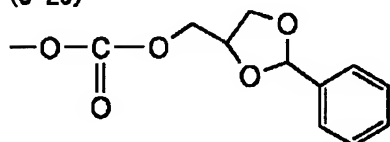
(U-23)



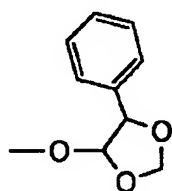
(U-24)



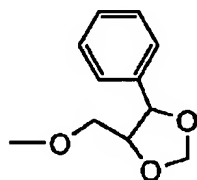
(U-25)



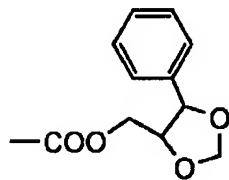
(U-26)



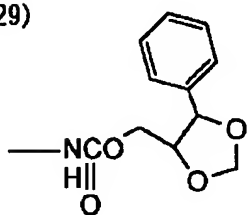
(U-27)



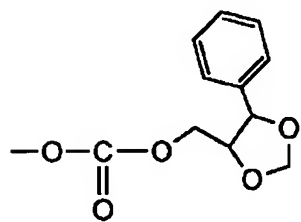
(U-28)



(U-29)



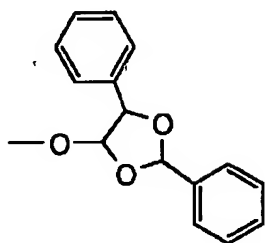
(U-30)



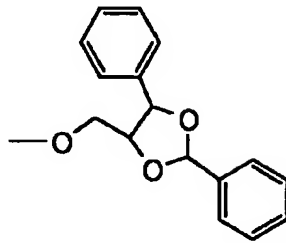
[0059]

[Formula 26]

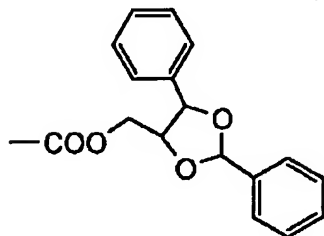
(U-31)



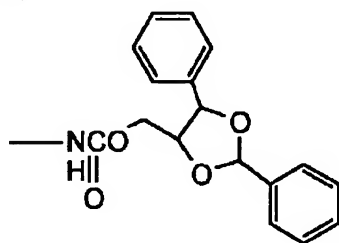
(U-32)



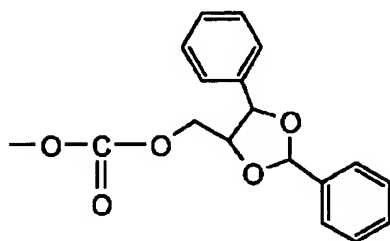
(U-33)



(U-34)



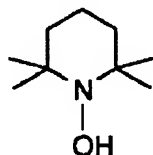
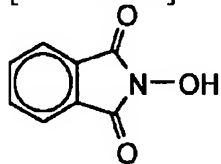
(U-35)



[0060] ** Although the example of these compounds is given to below about a compound, it is not limited to these.

[0061]

[Formula 27]



[0062] As a compound of these (a), the compound of above **, **, and ** is desirable, and the compound of ** and ** is still more desirable.

[0063] what a commercial thing can be suitably used for the compound of these (a), and is not marketing -- a law -- it is compoundable simple by the method. Moreover, although the molecular weight of the compound of (a) is 3000 or less, it is 2500 or less preferably and is 2000 or less still more preferably.

[0064] As an addition of the compound of (a) in the resist constituent of this invention, 0.5 - 50 % of the weight is desirable to all constituent weight (solid content), and it is 3 - 30 % of the weight more preferably.

[0065] [II] Compound which generates an acid by the exposure of the (b) energy line (henceforth "a component (b)") In addition, the above-mentioned energy line expresses the light, ultraviolet rays, an electron ray, or an X-ray. Although anything can be used if it is the compound which generates an acid by the exposure of an energy line as the above-mentioned (b) component, the compound expressed with the above-mentioned general formula (I) - (II) is desirable.

[0066] [II-1] In the compound general formula (I) expressed with a general formula (I) - (II) - (II), the thing of 1-4 carbon numbers like a methyl group, an ethyl group, a propyl group, n-butyl, sec-butyl, and t-butyl which may have a substituent is mentioned as the shape of a straight chain of R1-R22, and a letter alkyl group of branching. As an annular alkyl group, the thing of 3-8 carbon numbers like a cyclo propyl group, a cyclopentyl group, and a cyclohexyl radical which may have a substituent is mentioned. As the shape of a straight chain of R1-R23, and a letter alkoxy group of branching, the thing of 1-4 carbon numbers like a methoxy group, an ethoxy radical, a hydroxy ethoxy radical, a

propoxy group, an n-butoxy radical, an iso butoxy radical, a sec-butoxy radical, and a t-butoxy radical is mentioned, for example. As an annular alkoxy group, a cyclopenthyloxy radical and a cyclohexyloxy radical are mentioned, for example. As a halogen atom of R1 -R22, a fluorine atom, a chlorine atom, a bromine atom, and iodine atom can be mentioned. As an aryl group of R23, the thing of 6-14 carbon numbers which may have a phenyl group, a tolyl group, a methoxyphenyl radical, and a substituent like a naphthyl group, for example is mentioned.

[0067] The alkoxy group of 1-4 carbon numbers, a halogen atom (a fluorine atom, a chlorine atom, iodine atom), the aryl group of 6-10 carbon numbers, the alkenyl radical of 2-6 carbon numbers, a cyano group, a hydroxy group, a carboxy group, an alkoxy carbonyl group, a nitro group, etc. are mentioned preferably as these substituents.

[0068] Moreover, two or more of R1-R12, and R13-R22 can mention a furan ring, a dihydrofuran ring, a pyran ring, a trihydro pyran ring, a thiophene ring, a pyrrole ring, etc., for example as a ring containing one sort chosen from the single bond and carbon which are combined and formed, oxygen, sulfur, and nitrogen, or two sorts or more.

[0069] In a general formula (I) - (II), X- is the anion of a sulfonic acid. As an anion of a sulfonic acid, the anion of an alkyl sulfonic acid, benzenesulfonic acid, a naphthalene sulfonic acid, or an anthracene sulfonic acid etc. is mentioned.

[0070] In a general formula (I) - (II), the anion of the alkyl sulfonic acid which has as X- at least one sort chosen from the following radical, benzenesulfonic acid, a naphthalene sulfonic acid, or an anthracene sulfonic acid is desirable. at least one fluorine atom -- the shape of a straight chain permuted by one fluorine atom even if few -- the letter of branching, or an annular alkyl group -- the shape of a straight chain permuted by one fluorine atom even if few -- The letter of branching or an annular alkoxy group, if few the acyl group permuted by the fluorine atom of one **, if few the acyloxy radical permuted by the fluorine atom of one **, if few the sulfonyl group permuted by the fluorine atom of one **, if few the sulfonyloxy radical permuted by the fluorine atom of one ** -- the sulfonylamino radical permuted by one fluorine atom even if few -- the aryl group permuted by one fluorine atom even if few -- even if few, one fluorine atom permuted -- an aralkyl radical And the alkoxy carbonyl group permuted by at least one fluorine atom [0071] As the shape of an above-mentioned straight chain, the letter of branching, or an annular alkyl group, carbon numbers are 1-12 and what is permuted by 1-25 fluorine atoms is desirable. Specifically, a TORIFURORO methyl group, the Pentough Rollo ethyl group, 2 and 2, 2-TORIFURORO ethyl group, a heptaphloropropyl radical, a hepta-FURORO isopropyl group, perphloro butyl, a perphloro octyl radical, the perphloro dodecyl, a perphloro cyclohexyl radical, etc. can be mentioned. Especially, the perphloroalkyl group of the carbon numbers 1-4 altogether permuted with the fluorine is desirable.

[0072] As the shape of an above-mentioned straight chain, the letter of branching, or an annular alkoxy group, carbon numbers are 1-12 and what is permuted by 1-25 fluorine atoms is desirable. Specifically, a TORIFURORO methoxy group, a pen TAFURORO ethoxy radical, a hepta-FURORO isopropyloxy radical, a perphloro butoxy radical, a perphloro octyloxy radical, a perphloro dodecyloxy radical, a perphloro cyclohexyloxy radical, etc. can be mentioned. Especially, the perphloro alkoxy group of the carbon numbers 1-4 altogether permuted with the fluorine is desirable.

[0073] As the above-mentioned acyl group, carbon numbers are 2-12 and what is permuted by 1-23 fluorine atoms is desirable. Specifically, the Tori Flo Roar cetyl group, the Flo Roar cetyl group, a pen TAFURORO propionyl radical, the Pentough Rollo benzoyl, etc. can be mentioned.

[0074] As the above-mentioned acyloxy radical, carbon numbers are 2-12 and what is permuted by 1-23 fluorine atoms is desirable. Specifically, a TORIFURORO acetoxy radical, a FURORO acetoxy radical, a pen TAFURORO propionyloxy radical, a pen TAFURORO benzoyloxy radical, etc. can be mentioned.

[0075] As the above-mentioned sulfonyl group, carbon numbers are 1-12 and what is permuted by 1-25 fluorine atoms is desirable. Specifically, a truffe ROROME tongue sulfonyl group, the Pentough ROROE tongue sulfonyl group, a perphloro butane sulfonyl group, a perphloro octane sulfonyl group, a pen TAFURORO benzenesulphonyl radical, 4-trifluoromethylbenzene sulfonyl group, etc. can be mentioned.

[0076] As the above-mentioned sulfonyloxy radical, carbon numbers are 1-12 and what is permuted by 1-25 fluorine atoms is desirable. Specifically, truffe ROROME tongue sulfonyloxy, a perphloro butane sulfonyloxy radical, 4-trifluoromethylbenzene sulfonyloxy radical, etc. can be mentioned.

[0077] As the above-mentioned sulfonylamino radical, carbon numbers are 1-12 and what is permuted by 1-25 fluorine atoms is desirable. Specifically, a truffe ROROME tongue sulfonylamino radical, a perphloro butane sulfonylamino radical, a perphloro octane sulfonylamino radical, a pen TAFURORO benzenesulphonyl amino radical, etc. can be mentioned.

[0078] As the above-mentioned aryl group, carbon numbers are 6-14 and what is permuted by 1-9 fluorine atoms is

desirable. Specifically, Pentough Rollo phenyl group, 4-truffe ROROME chill phenyl group, hepta-FURORO naphthyl group, nona FURORO anthranil, 4-FURORO phenyl group, 2, and 4-JIFURORO phenyl group etc. can be mentioned. [0079] As the above-mentioned aralkyl radical, carbon numbers are 7-10 and what is permuted by 1-15 fluorine atoms is desirable. Specifically, a pen TAFURORO phenylmethyl radical, a pen TAFURORO phenylethyl radical, perphloro benzyl, a perphloro phenethyl radical, etc. can be mentioned.

[0080] As the above-mentioned alkoxy carbonyl group, carbon numbers are 2-13 and what is permuted by 1-25 fluorine atoms is desirable. Specifically, a TORIFURORO methoxycarbonyl group, a pen TAFURORO ethoxycarbonyl radical, a pen TAFURORO phenoxy carbonyl group, a perphloro butoxycarbonyl radical, a perphloro octyloxy carbonyl group, etc. can be mentioned.

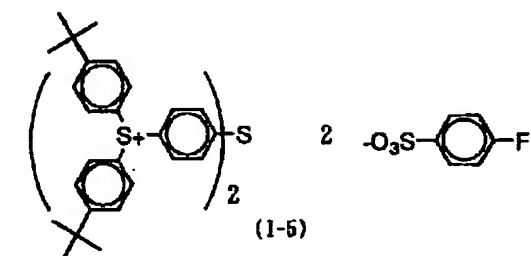
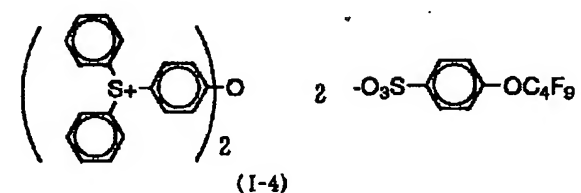
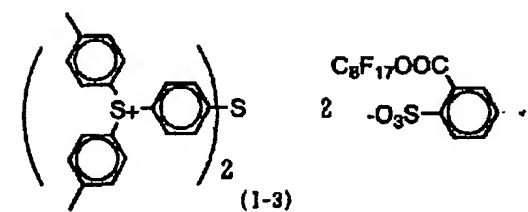
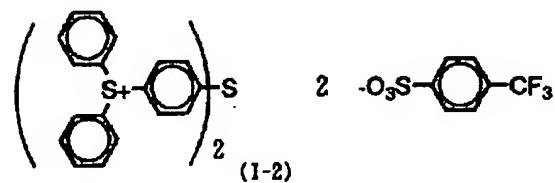
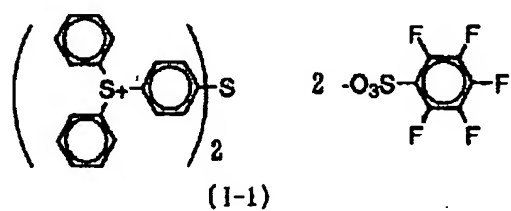
[0081] As most desirable X-, it is a fluorine permutation benzenesulfonic acid anion.

[0082] Moreover, the alkyl sulfonic acid which has the above-mentioned fluorine-containing substituent, benzenesulfonic acid, a naphthalene sulfonic acid, or an anthracene sulfonic acid may be further permuted by the shape of a straight chain, the letter of branching or an annular alkoxy group, an acyl group, an acyloxy radical, a sulfonyl group, a sulfonyloxy radical, a sulfonylamino radical, an aryl group, an aralkyl radical, the alkoxy carbonyl group (these carbon number range is the same as that of the aforementioned thing), the halogen (except for a fluorine), the hydroxyl group, a nitro group, etc.

[0083] The example of a compound expressed with a general formula (I) is shown below.

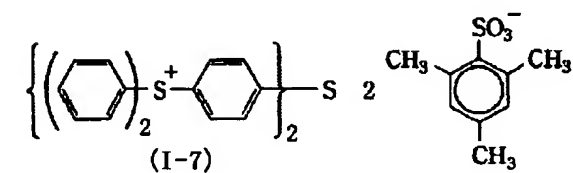
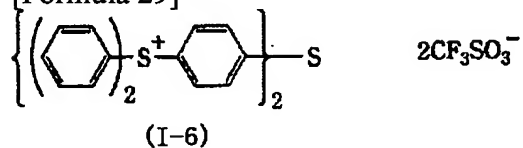
[0084]

[Formula 28]



[0085]

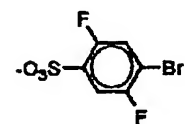
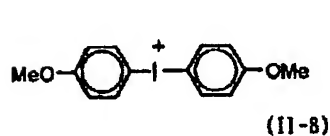
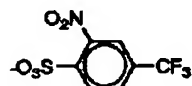
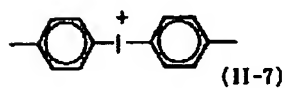
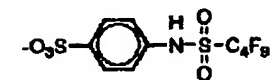
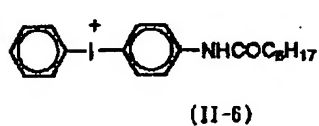
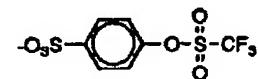
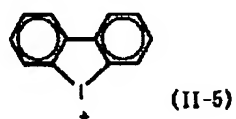
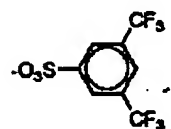
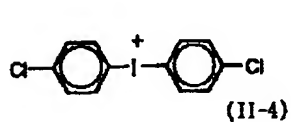
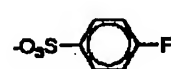
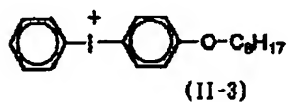
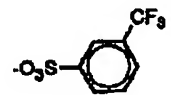
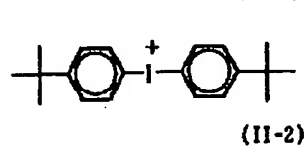
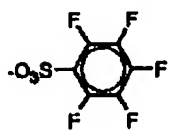
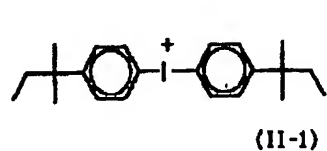
[Formula 29]



[0086] The example of a compound expressed with a general formula (II) is shown below.

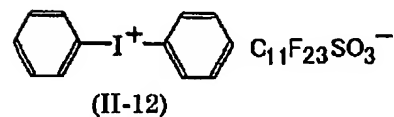
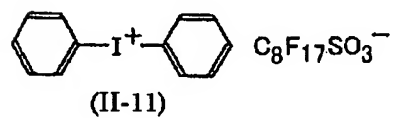
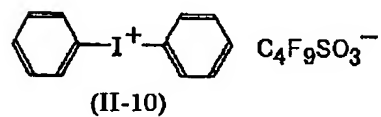
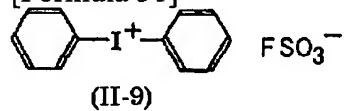
[0087]

[Formula 30]



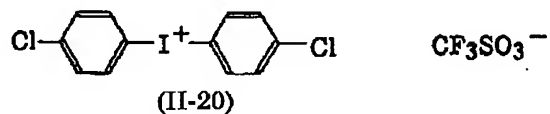
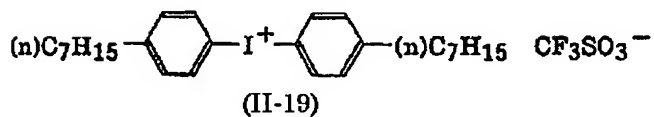
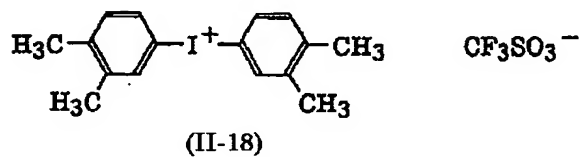
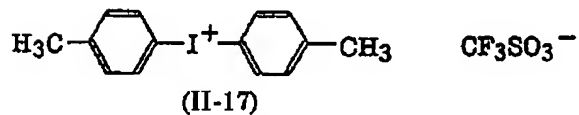
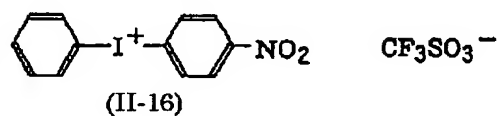
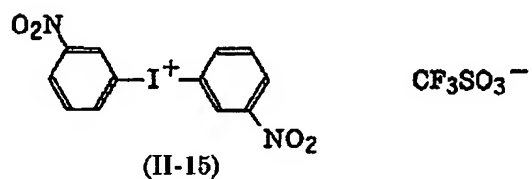
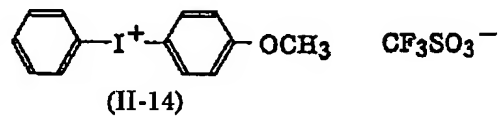
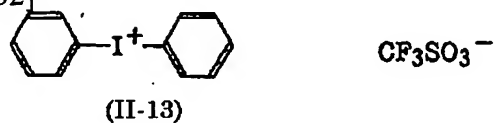
[0088]

[Formula 31]



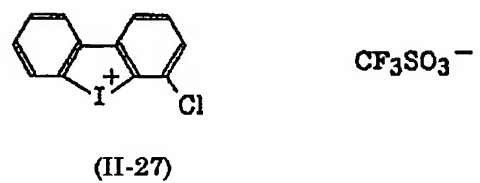
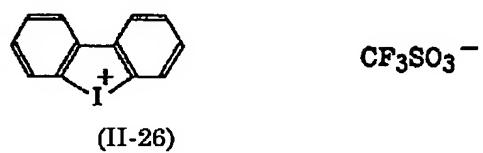
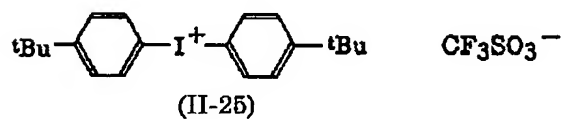
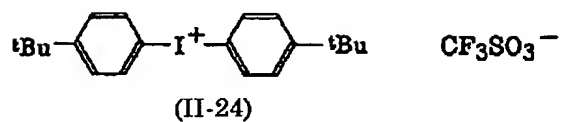
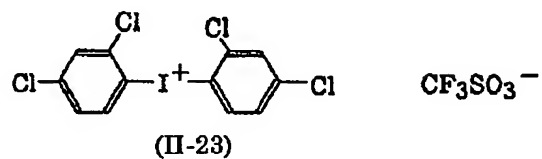
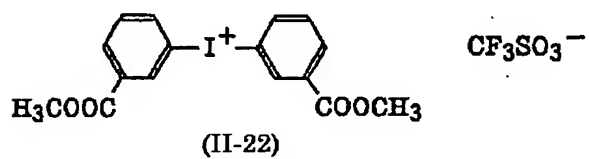
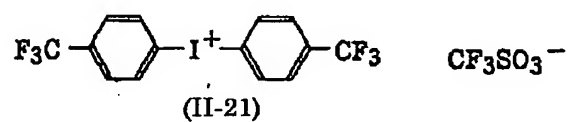
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[Formula 32]

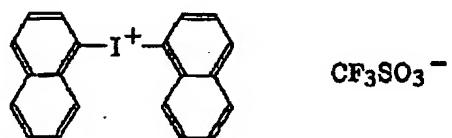


[0090]

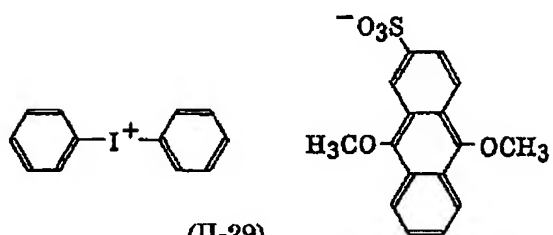
[Formula 33]



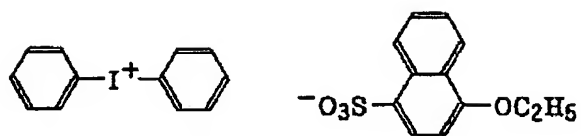
[0091]
[Formula 34]



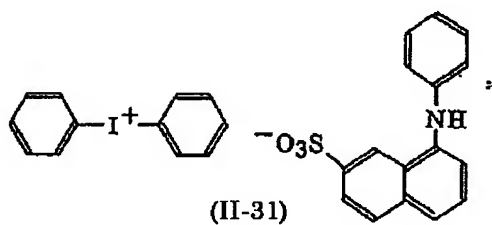
(II-28)



(II-29)

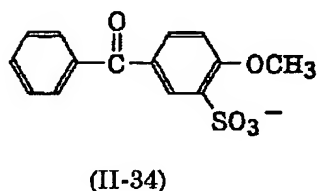
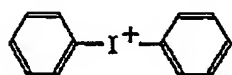
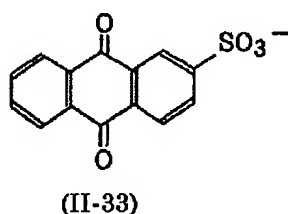
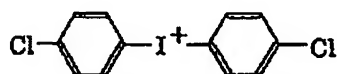
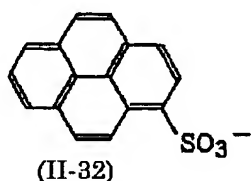
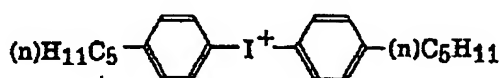


(II-30)



(II-31)

[0092]
[Formula 35]



[0093] One sort or two sorts or more may be used together and used for the compound expressed with a general formula (I) - (II).

[0094] The compound of a general formula (I) For example, aryl Grignard reagents, such as aryl magnesium bromide, How to carry out salt exchange of the triarylsulfonium halide which the phenyl sulfoxide which is not permuted [a permutation or] was made to react, and was obtained with a corresponding sulfonic acid, Acid catalysts, such as methansulfonic acid / diphosphorus pentaoxide, or an aluminum chloride, are used for the phenyl sulfoxide which is not permuted [a permutation or] and a corresponding aromatic compound. Condensation, The approach of carrying out salt exchange or a diaryl iodonium salt, and a diaryl sulfide are compoundable by condensation, the approach of carrying out salt exchange, etc. using catalysts, such as copper acetate. The compound of a formula (II) is compoundable by making an aromatic compound react using a periodate. Moreover, the sulfonic acid or sulfonate used for salt exchange can be obtained by the approach of hydrolyzing commercial sulfonic-acid chloride, the approach of reacting an aromatic compound and a chlorosulfonic acid, the approach of reacting an aromatic compound and sulfamic acid, etc.

[0095] The synthetic approach of the concrete compound of a general formula (I) - (II) is shown below concretely. (Composition of a ** NTAFUORO benzenesulfonic acid tetramethylammonium salt) Pentough ROROPENSEN sulfonyl chloride 25g was dissolved in methanol 100ml under ice-cooling, and 100g of tetramethylammonium hydroxide water solutions was slowly added to this 25%. When stirred at the room temperature for 3 hours, the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt was obtained. This solution was used for the salt exchange with sulfonium salt and iodonium salt.

[0096] (Composition of triarylsulfonium Pentough ROROBENSEN sulfonate: Composition of an example (I-a) and the mixture of (I-1))

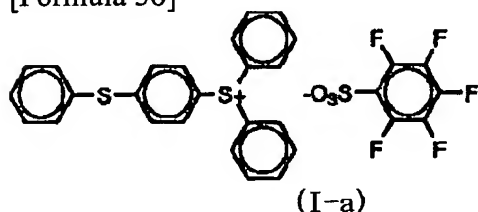
If triarylsulfonium chloride 50g (the product made from Fluka, triphenylsulfonium chloride 50% water solution) is

dissolved in 1 500m of water and the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt of an excessive amount is added to this, oil has deposited. When the oil obtained except for the supernatant was rinsed and it dried by decant, triarylsulfonium Pentough Rollo ** NSEN sulfonate (let an example (I-a) and (I-1) be principal components) was obtained.

[0097] The structure expression of (I-a) of the above-mentioned publication is shown below.

[0098]

[Formula 36]



[0099] (Composition of JI (4-t-amyl phenyl) iodonium Pentough ROROBENSEN sulfonate: Composition of an example (II-1))

t-amyl benzene 60g, 39.5g of potassium iodates, 81g of acetic anhydrides, and dichloromethane 170ml were mixed, and 66.8g of bottom concentrated sulfuric acid of ice-cooling was slowly dropped at this. After stirring under ice-cooling for 2 hours, it stirred at the room temperature for 10 hours. 1 was added to reaction mixture 500m of water under ice-cooling, and when it condensed after it washed this by dichloromethane and a sodium hydrogencarbonate and water washed the extract and the organic phase, the JI (4-t-amyl phenyl) iodonium sulfate was obtained. This sulfate was added to the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt of an excessive amount. 1 was added to this solution 500m of water, and when it condensed after it washed this by dichloromethane and a tetramethylammonium hydroxide water solution and water washed the extract and the organic phase 5%, JI (4-t-amyl phenyl) iodonium Pentough ROROBENSEN sulfonate was obtained. It is compoundable by using an approach with the same said of other compounds.

[0100] [II-2] In other acid generator this inventions which can be used as a component (b), the compound which decomposes into below by the exposure of an energy line of a publication as a component (b), and generates an acid can also be used. Moreover, in this invention, the compound which decomposes by the exposure of the following energy lines and generates an acid as a component (b) with the compound expressed with the above-mentioned general formula (I) - a general formula (II) may be used together.

[0101] the amount of the acid generator used which can be used together with the compound expressed with the above-mentioned general formula (I) in this invention - a general formula (II) -- a mole ratio (acid generator of compound/expressed with a general formula (I) - a general formula (II), and others) -- it is -- usually -- 100 / 0 - 20/80 - desirable -- 100 / 0 - 40/60 -- it is 100 / 0 - 50/50 still more preferably. The total content of a component (b) is 0.1 - 20 % of the weight usually 1 - 7 % of the weight still more preferably 0.5 to 10% of the weight preferably to the solid content of the positive type chemistry magnification resist constituent all constituent of this invention.

[0102] The well-known compounds which generate an acid as such an acid generator by the exposure of the electron ray or X-ray currently used for the photoinitiator of optical cationic polymerization, the photoinitiator of an optical radical polymerization, the optical decolorizing agent of coloring matter, optical alterant, or a micro resist, and those mixture can be used choosing them suitably.

[0103] For example S.I.Schlesinger, Photogr.Sci.Eng., 18,387 (1974), T. Diazonium salt given in S.Bal etal, Polymer, 21,423 (1980), etc., U.S. Pat. No. 4,069,055, said 4,069,056 numbers, ** Re No. 27,992, 17 Ammonium salt given in Japanese Patent Application No. No. 140,140 [three to] etc., D.C.Necker etal, Macromolecules, 2468 (1984), C. S.Wenetal, Teh, Proc.Conf.Rad.Curing ASIA, p478 Tokyo, Oct (1988), Phosphonium salt given in U.S. Pat. No. 4,069,055, said 4,069,056 numbers, etc., J. V.Crivello etal, Macromolecules, 10 (6), 1307 (1977), Chem.&Eng:News, Nov.28, p31 (1988), The Europe patent No. 104,143, U.S. Pat. No. 339,049, 410,201, Iodonium salt given in JP,2-150,848,A, JP,2-296,514,A, etc., J. -- V.Crivello etal and Polymer J. -- 17 and 73 (1985) -- J. 43 V.Crivelloetal.J.Org.Chem., 3055 (1978), W. 22 R.Watt etal, J.Polymer Sci., Polymer Chem.Ed., 1789 (1984), J. V.Crivello etal, Polymer Bull., 14,279 (1985), J. V.Crivello etal, Macromolecules, 14 (5), 17 1141 (1981), J.V.Crivello etal, J.Poly merSci., Polymer Chem.Ed., 2877 (1979), Europe patent 370,693rd A number, **, and 902,114 A number,

said 233,567 numbers, Said 297,443 numbers, said 297,442 numbers, United States patent 4,933rd, and No. 377, said -- No. 161,811 -- said -- No. 410,201 -- said -- No. 339,049 -- said -- No. 4,760,013 said -- No. 4,734,444 -- said -- 2,833,827 A number and the Germany patent No. 2,904,626 Sulfonium salt given in said 3,604,580 numbers, said 3,604,581 numbers, etc., J. V. Crivello et al, Macromolecules, 10 (6), 1307 (1977), J.V. Crivello et al, J. Polymer Sci., Polymer Chem. Ed., 17, and 1047 (1979) etc. -- the seleno NIUMU salt of a publication -- C. -- S. Wen et al, Teh, Proc. Conf. Rad. Curing ASIA, p478 Tokyo, and Oct (1988) etc. -- onium salt, such as arsonium salt of a publication, -- U.S. Pat. No. 3,905,815, JP,46-4605,B, JP,48-36281,A, JP,55-32070,A, JP,60-239736,A, JP,61-169835,A, JP,61-169837,A, JP,62-58241,A, JP,62-212401,A, An organic halogenated compound given in JP,63-70243,A, JP,63-298339,A, etc., KMeier et al, J. Rad. Curing, 13 (4), 26 (1986), T.P. Gill et al, Inorg. Chem., and 19 and 3007 (1980), D. Astruc, Acc. Chem. Res., 19 (12), 377 (1986), It is an account to JP,2-161445,A etc. The organic metal / organic halogenide of **, S. Hayase et al, J. Polymer Sci., 25,753 (1987), E. 23 Reichmanis et al, J. Polymer Sci., Polymer Chem. Ed., 1 (1985), Q. Q. Zhu et al, J. Photochem., 36, 85, 39,317 (1987), B. Amit et al, Tetrahedron Lett., (24) 2205 (1973), D.H.R. Barton et al, J. Chem. Soc., 3571 (1965), P. M. Collins et al, J. Chem. Soc., Perkin I, 1695 (1975), M. Rudinstein et al, Tetrahedron Lett., (17), 110 1445 (1975), J.W. Walker et al, J. Am. Chem. Soc., 7170 (1988), S.C. Busman et al, J. Imaging Technol., 11 (4), 21 191 (1985), H.M. Houlihan et al, Macromolecules, 2001 (1988), P. M. Collins et al, J. Chem. Soc., Chem. Commun., 532 (1972), S. 18 Hayase et al, Macromolecules, 1799 (1985), E. Reichmanis et al, J. Electrochem. Soc., Solid State Sci. Technol., 130 (6), F. 21 M. Houlihan et al, Macromolecules, 2001 (1988), the Europe patent 0290th and No. 750 -- said -- No. 046 or 083 -- said -- No. 156 or 535 said -- No. 271,851 -- said -- 0,388,343 Number, U.S. Pat. No. 3,901,710 -- The photo-oxide generating agent which has o-nitrobenzyl mold protective group of a publication in said 4,181,531 numbers, JP,60-198538,A, JP,53-133022,A, etc., M. TUNOOKA et al, Polymer Preprints Japan, 35 (8), G. Berner et al, J. Rad. Curing, 13 (4), W. J. Mijs et al, Coating Technol., 55 (697) and 45 (1983), Akzo, H. Adachi et al, Polymer Preprints, Japan, 37 (3), the Europe patent 0199th and No. 672 -- said -- No. 84515 -- said -- No. 199 or 672 -- said -- No. 044 or 115 -- said -- No. 0101 or 122 and U.S. Pat. No. 618,564 -- said -- No. 4,371,605, said -- No. 4,431,774, JP,64-18143,A, JP,2-245756,A, Japanese Patent Application No. No. 140109 [three to], etc. The disulfon compound of a publication can be mentioned to the compound which generates the sulfonic acid represented by the imino sulfonate of a publication etc., JP,61-166544,A, etc.

[0104] moreover, the radical which generates an acid by the exposure of these energy lines or the compound which introduced the compound into the principal chain or side chain of a polymer -- for example M. E. Woodhouse 104 et al, J. Am. Chem. Soc., 5586 (1982), S. P. Pappas et al, J. Imaging Sci., 30 (5), 218 (1986), S. Kondo et al, Makromol. Chem., Rapid Commun., 9,625 (1988), . Yamada et al, Makromol. Chem., and 152,153,163 (1972), J. 17 V. Crivello et al, J. Polymer Sci., Polymer Chem. Ed., 3845 (1979), U.S. Pat. No. 3,849,137, the Germany patent No. 3914407, JP,63-26653,A, The compound of a publication can be used for JP,55-164824,A, JP,62-69263,A, JP,63-146038,A, JP,63-163452,A, JP,62-153853,A, JP,63-146029,A, etc.

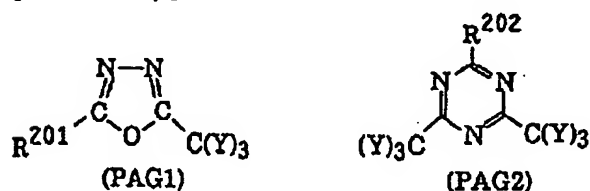
[0105] Furthermore, the compound which generates the acid of a publication can also be used for V.N.R. Pillai, Synthesis, (1), 1 (1980), A. Abad et al, Tetrahedron Lett., (47) 4555 (1971), D.H.R. Barton et al, J. Chem. Soc., (C), 329 (1970), U.S. Pat. No. 3,779,778, the Europe patent No. 126,712, etc.

[0106] In the compound which decomposes by the exposure of the energy line in which the above-mentioned concomitant use is possible, and generates an acid, especially the thing used effectively is explained below.

(1) S-triazine derivative expressed with the oxazole derivative or general formula (PAG2) expressed with the following general formula (PAG1) which the trihalomethyl group permuted.

[0107]

[Formula 37]

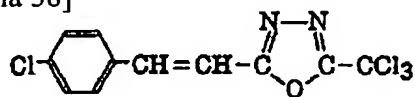


[0108] The inside of a formula, and R201 The aryl group which is not permuted [a permutation or], an alkenyl radical, and R202 The aryl group which is not permuted [a permutation or], an alkenyl radical, an alkyl group, and -C(Y)3 are

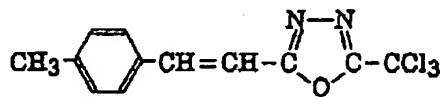
shown. Y shows a chlorine atom or a bromine atom. Although the following compounds can specifically be mentioned, it is not limited to these.

[0109]

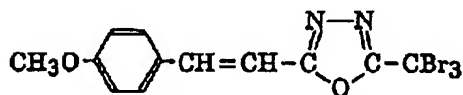
[Formula 38]



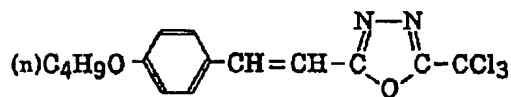
(PAG1-1)



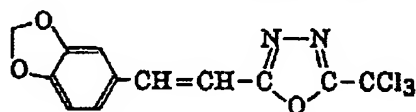
(PAG1-2)



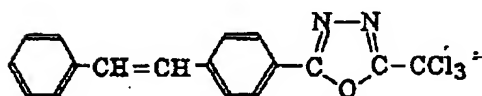
(PAG1-3)



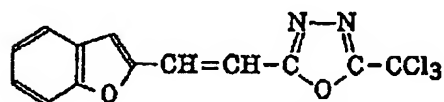
(PAG1-4)



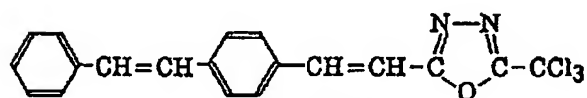
(PAG1-5)



(PAG1-6)



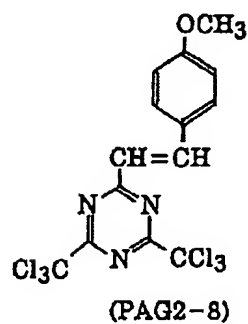
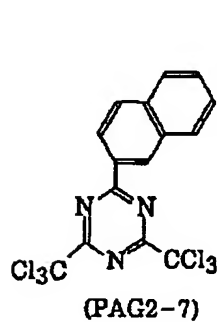
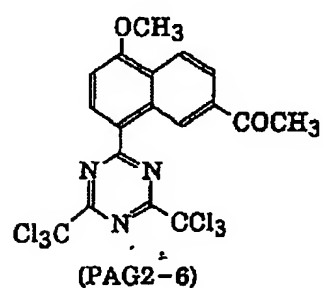
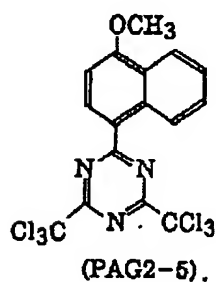
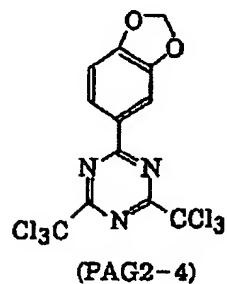
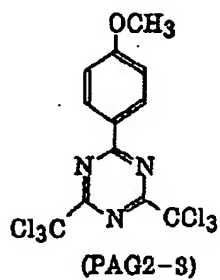
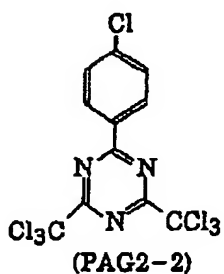
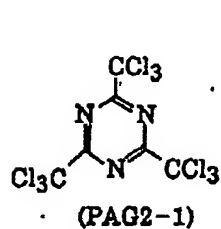
(PAG1-7)



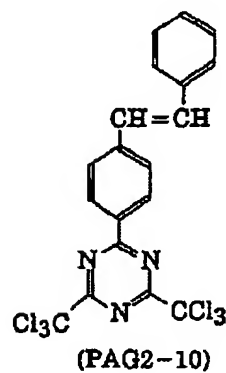
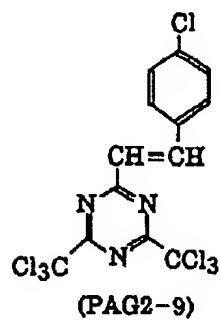
(PAG1-8)

[0110]

[Formula 39]

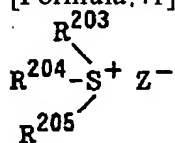


[0111]
[Formula 40]



[0112] (2) Sulfonium salt expressed with a general formula (PAG4).

[0113]
[Formula.41]



(PAG4)

[0114] R203, R204, and R205 The alkyl group which is not permuted [a permutation or] and an aryl group are shown independently respectively. Preferably, they are the aryl group of carbon numbers 6-14, the alkyl groups of carbon numbers 1-8, and those permutation derivatives. As a desirable substituent, it is the alkoxy group of carbon numbers 1-8, the alkyl group of carbon numbers 1-8, a nitro group, a carboxyl group, a HIRODOKISHI radical, and a halogen atom to an aryl group, and they are the alkoxy group of carbon numbers 1-8, a carboxyl group, and an ARUKOSHIKI carbonyl group to an alkyl group.

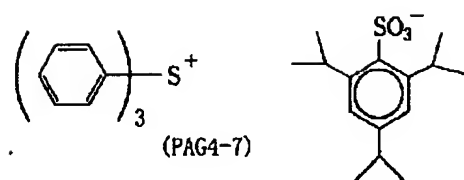
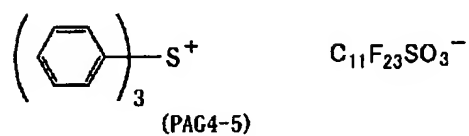
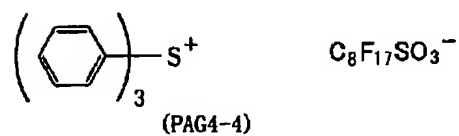
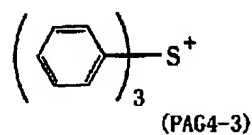
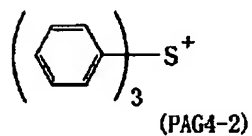
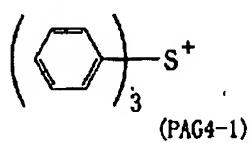
[0115] Z- shows an opposite anion, for example, is condensation polykaryotic aromatic series sulfonic-acid anions, such as perfluoro alkane sulfonic-acid anions, such as BF₄⁻ and CF₃SO₃⁻, and a naphthalene-1-sulfonic-acid anion, and an anthraquinone sulfonic acid. Although an anion, a sulfonic group content color, etc. can be mentioned, it is not limited to these.

[0116] Moreover, R203, R204, and R205 Two may be combined through each single bond or substituent.

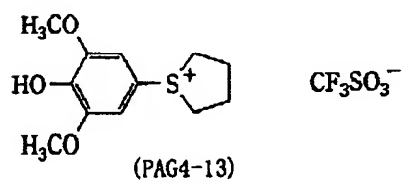
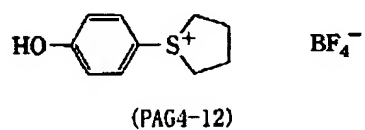
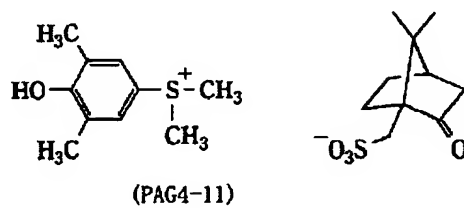
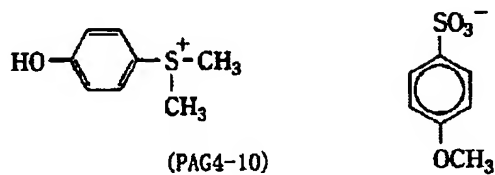
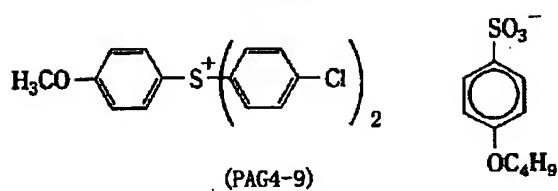
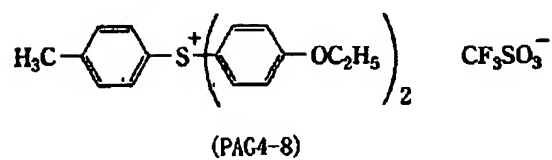
[0117] Although the compound shown below as an example is mentioned, it is not limited to these.

[0118]

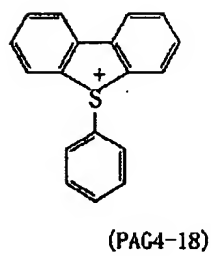
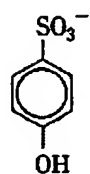
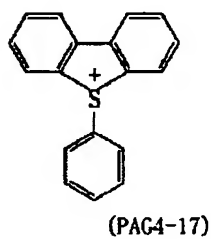
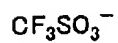
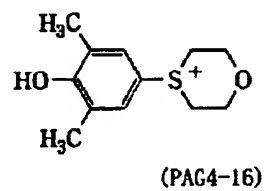
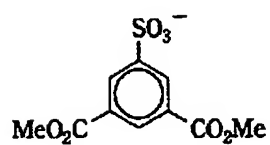
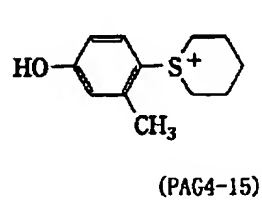
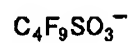
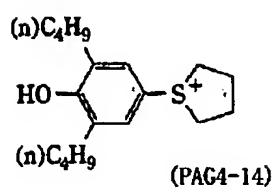
[Formula 42]



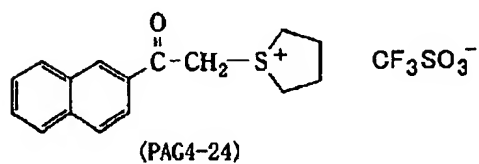
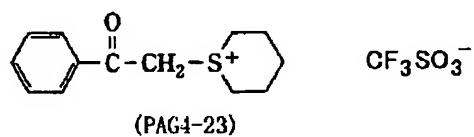
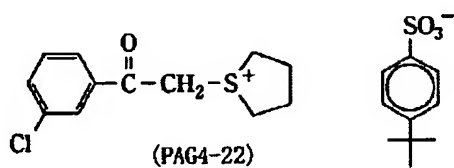
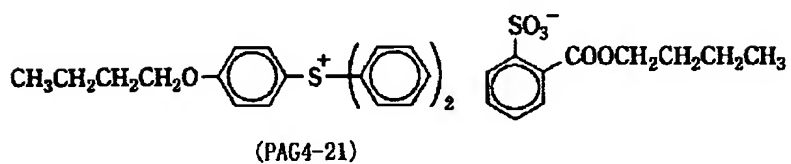
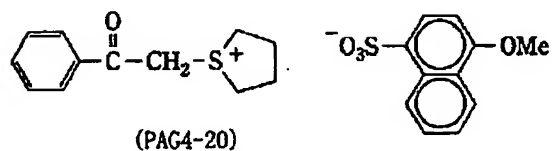
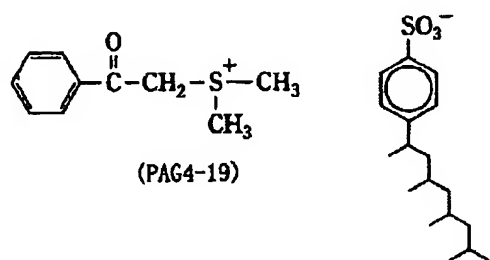
[0119]
[Formula 43]



[0120]
[Formula 44]

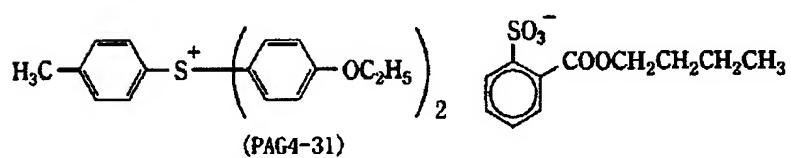
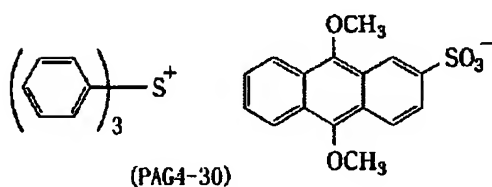
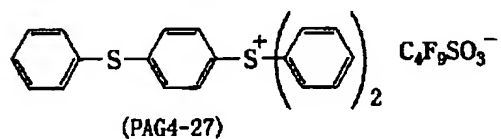
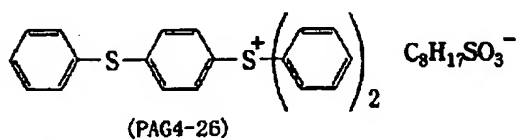
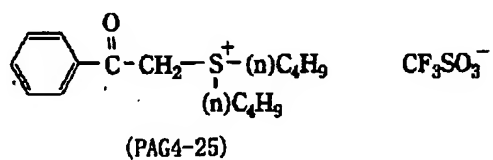


[0121]
 [Formula 45]



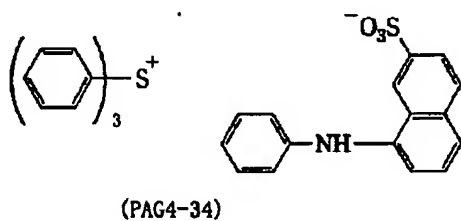
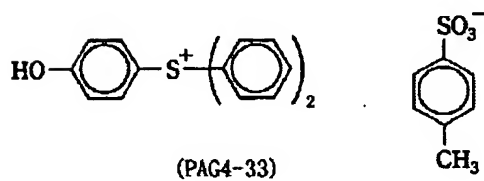
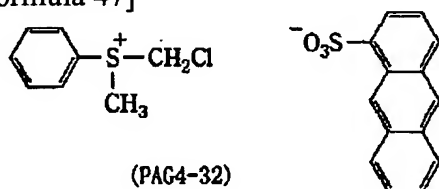
[0122]

[Formula 46]



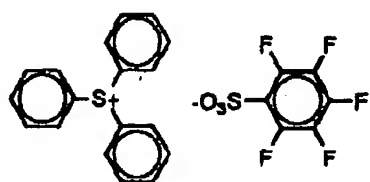
[0123]

[Formula 47]

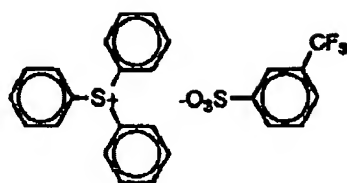


[0124]

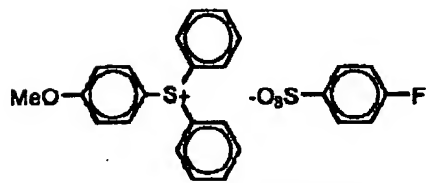
[Formula 48]



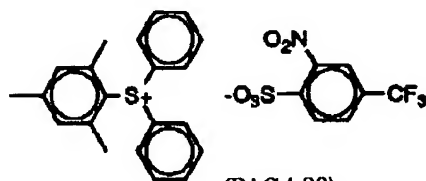
(PAG4-35)



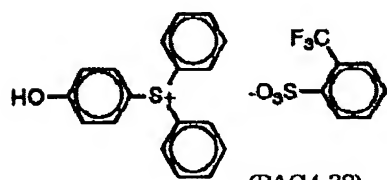
(PAG4-36)



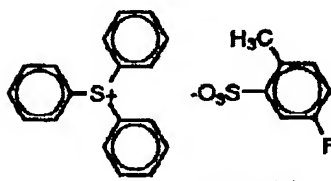
(PAG4-37)



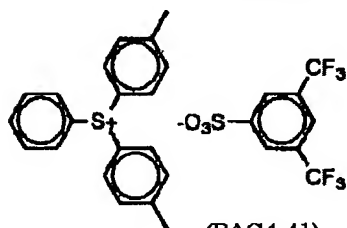
(PAG4-38)



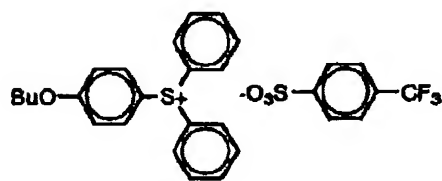
(PAG4-39)



(PAG4-40)

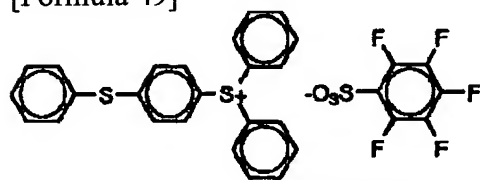


(PAG4-41)

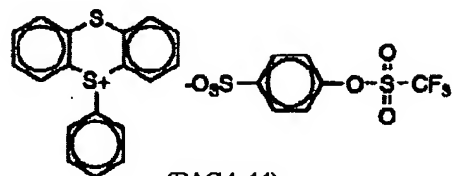


(PAG4-42)

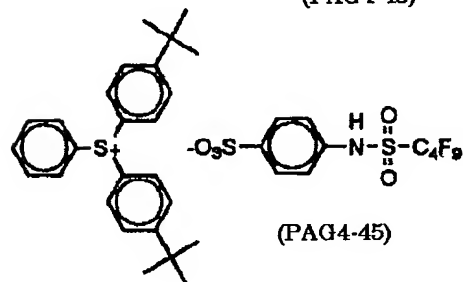
[0125]
[Formula 49]



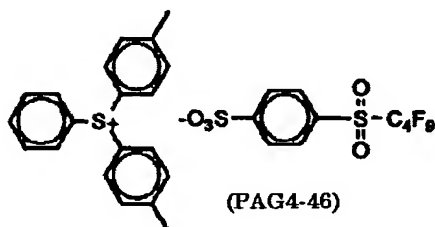
(PAG4-43)



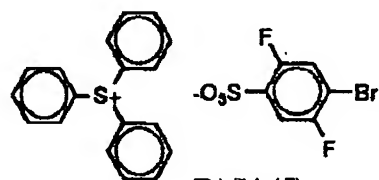
(PAG4-44)



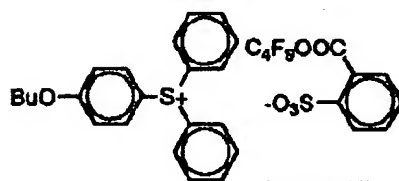
(PAG4-45)



(PAG4-46)



(PAG4-47)



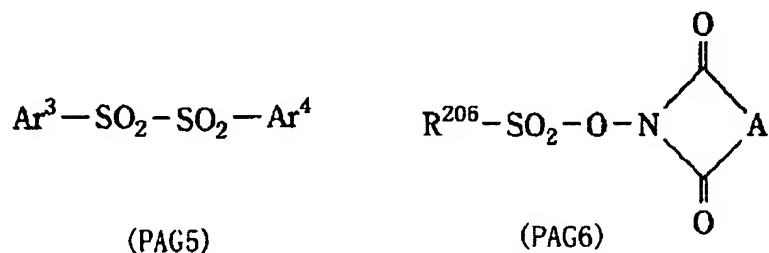
(PAG4-48)

[0126] For example, J.W.Knapczyk et al, J.Am.Chem.Soc., 91,145 (1969), the above-mentioned onium salt shown by the general formula (PAG4) is well-known. A. (L.Maycok et al, J.Org.Chem., 35 and 2532, 1970), E. Goethas et al, Bull.Soc.Chem.Belg., and 73 and 546 (1964), H. 51 M.Leicester, J.Ame.Chem.Soc., 3587 (1929), J. It is compoundable by the approach of a publication to V.Crivello et al, J.Polym.Chem.Ed., 18 and 2677 (1980), U.S. Pat. No. 2,807,648 and said 4,247,473 numbers, JP,53-101,331,A, etc.

[0127] (3) The imino sulfonate derivative expressed with the disulfon derivative or general formula (PAG6) expressed with the following general formula (PAG5).

[0128]

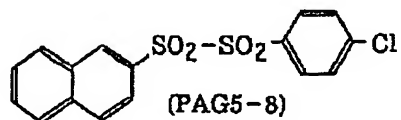
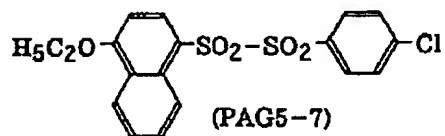
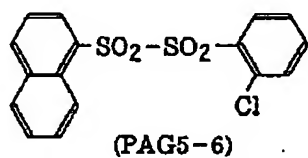
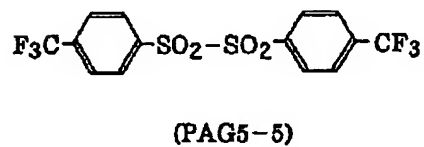
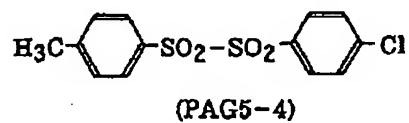
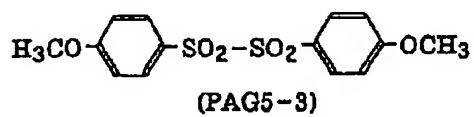
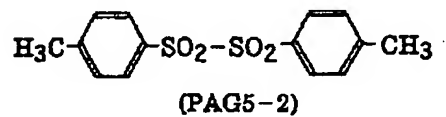
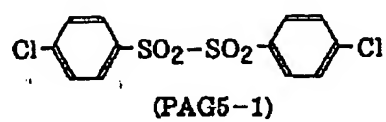
[Formula 50]



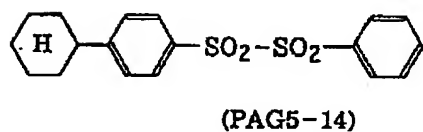
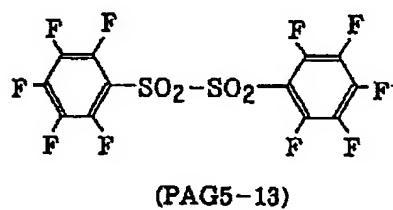
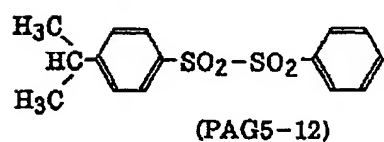
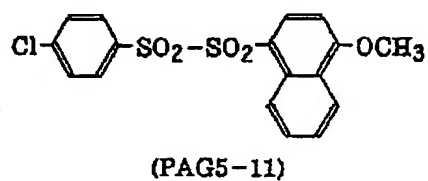
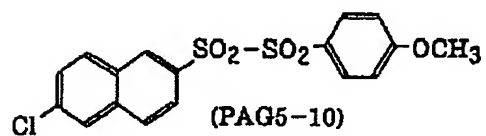
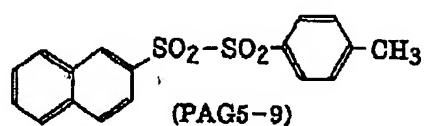
[0129] Ar3 and Ar4 show respectively the aryl group which is not permuted [a permutation or] independently among a formula. R206 The alkyl group which is not permuted [a permutation or] and an aryl group are shown. A shows the alkylene group which is not permuted [a permutation or], an alkenylene group, and an arylene radical. Although the compound shown below as an example is mentioned, it is not limited to these.

[0130]

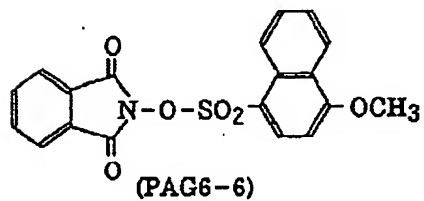
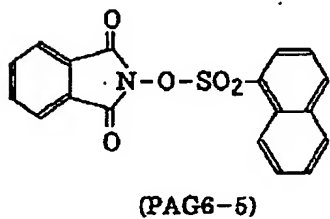
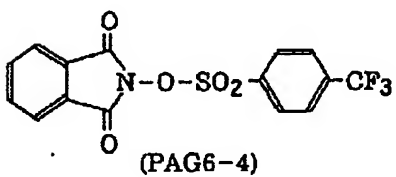
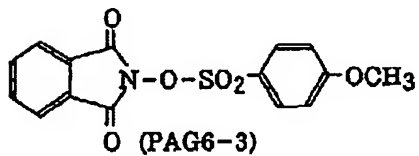
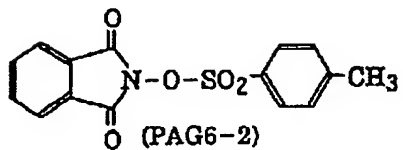
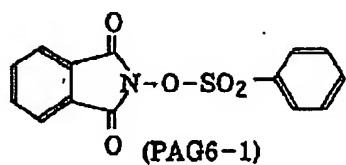
[Formula 51]



[0131]
[Formula 52]

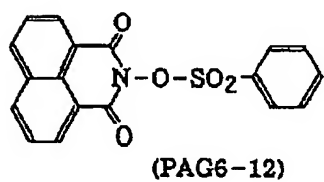
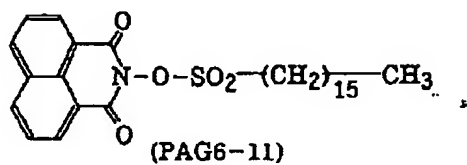
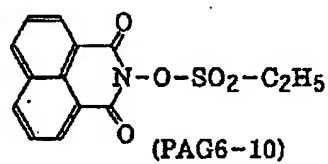
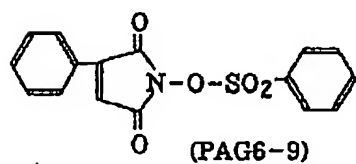
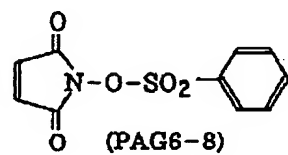
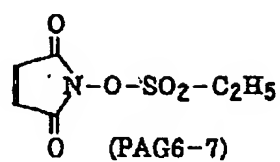


[0132]
[Formula 53]

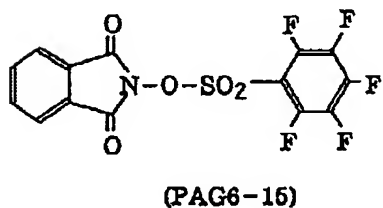
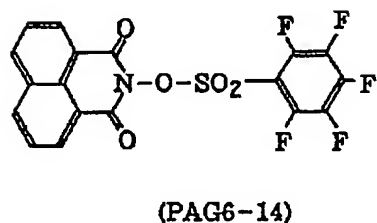
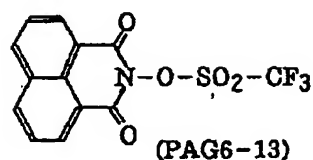


[0133]

[Formula 54]



[0134]
[Formula 55]



[0135] In this invention, although anything can be used if it is the compound which generates an acid by the exposure of an energy line as a component (b), it is desirable that reduction potential is more than -0.5V (vs S C E). the evaluation approach of reduction potential -- an electrochemistry measuring method (above) -- and (below) (Gihodo Shuppan, 1984) -- etc. -- the approach indicated can be used.

[0136] The resin to which it has the radical which may be decomposed with the (d) acid in this invention, and the solubility over an alkali developer increases according to an operation of an acid It has the radical which may be decomposed with ("component (d)" being said hereafter) or the (e) acid. It is desirable to contain either at least among the with a molecular weight of 3000 or less low-molecular lysis inhibition compounds (henceforth "a component (e)") to which the solubility over an alkali developer increases according to an operation of an acid.

[0137] [III] It is resin which has the radical which may be decomposed with the (e) acid and has the radical which may be decomposed into both the principal chain of resin, a side chain or a principal chain, and a side chain from an acid as a component (e) used in the positive type chemistry magnification resist constituent of resin this invention to which the solubility over an alkali developer increases according to an operation of an acid. Among this, the resin which has the radical which may be decomposed from an acid in a side chain is more desirable. Radicals desirable as a radical which may be decomposed from an acid are -COOA0 and zero -O-B, and the radical shown by -R0-COOA0 or -Ar-O-B0 is mentioned as a radical which contains these further. A0 shows -C (R01) (R02) (R03), -Si (R01) (R02) (R03), or 06 -C (R04) (R05)-O-R here. B0 A0 Or zero -CO-O-A is shown (R0, R01- the thing and homonymy of the after-mentioned [R06 and Ar]).

[0138] They are a silyl ether group, a cumyl ester group, an acetal radical, a tetrahydropyranyl ether group, an enol ether group, an enol ester group, the alkyl ether radical of the 3rd class, the alkyl ester group of the 3rd class, the alkyl carbonate radical of the 3rd class, etc. preferably as an acidolysis nature machine. Furthermore, they are the 3rd class alkyl ester group, the 3rd class alkyl carbonate radical, a cumyl ester group, an acetal radical, and a tetrahydropyranyl ether group preferably.

[0139] Next, as parent resin in case the radical which may be decomposed from these acids joins together as a side chain, it is a side chain. - They are OH or -COOH, and alkali fusibility resin that has a -R0-COOH or -Ar-OH radical preferably. For example, the alkali fusibility resin mentioned later can be mentioned.

[0140] The alkali dissolution rate of these alkali fusibility resin is measured by 0.261-N tetramethylammonium hydroxide (TMAH) (23 degrees C), and its thing 170A / more than a second is desirable. It is a thing 330A / more than a second especially preferably (A is angstrom). From such a viewpoint, especially desirable alkali fusibility resin is a part of o-, m-, p-Pori (hydroxystyrene) and these copolymers, hydrogenation Pori (hydroxystyrene), halogen or

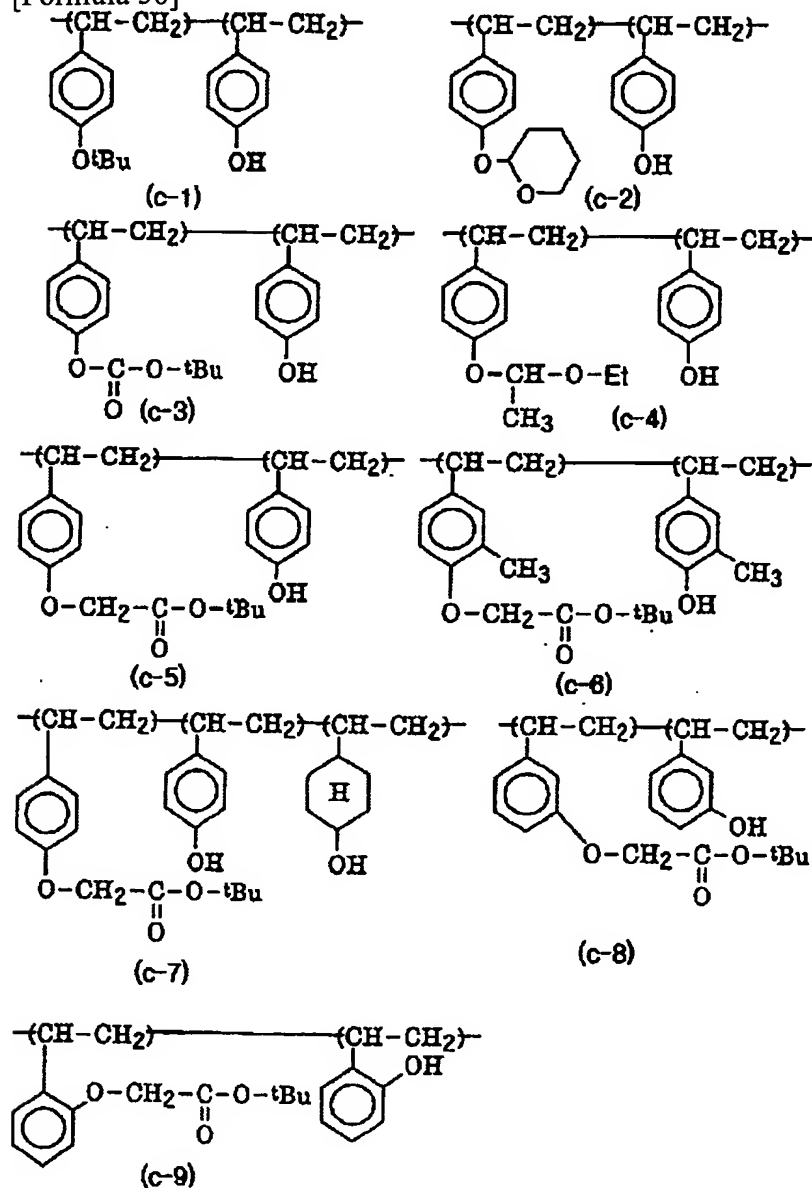
alkylation Pori (hydroxystyrene), Pori (hydroxystyrene), O-alkylation or O-acylation object, a styrene-hydroxystyrene copolymer, an alpha-methyl-styrene-hydroxystyrene copolymer, and hydrogenation novolak resin.

[0141] The component (e) used for this invention makes the precursor of the radical which may be decomposed from an acid react to alkali fusibility resin, or copolymerizes the alkali fusibility resin monomer which the radical which may be decomposed from an acid combined with various monomers, and can obtain it as indicated by Europe JP,254853,B, JP,2-25850,A, 3-223860, 4-251259, etc.

[0142] Although the example of the component (e) used for this invention is shown below, it is not limited to these.

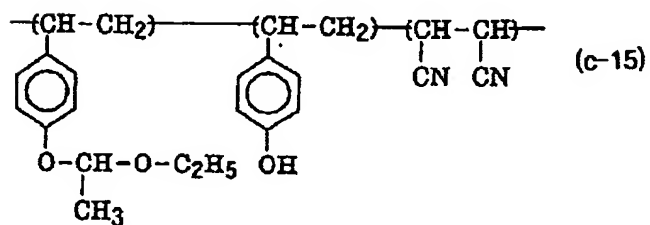
[0143]

[Formula 56]

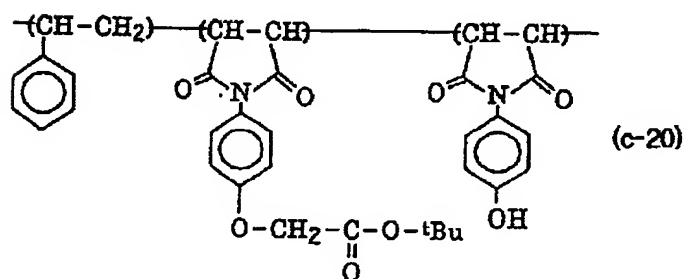
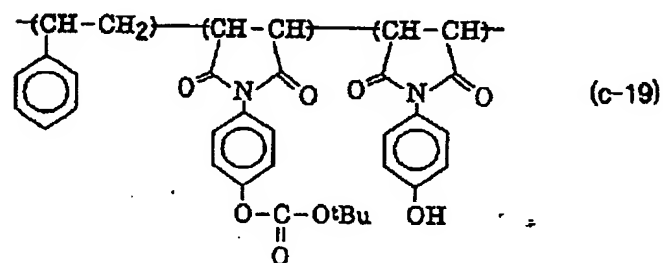
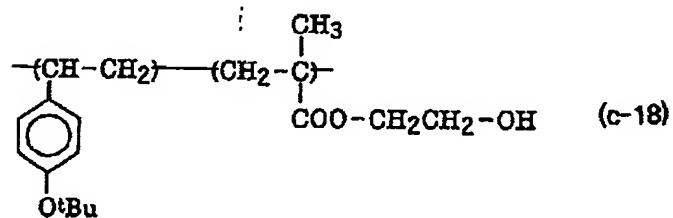
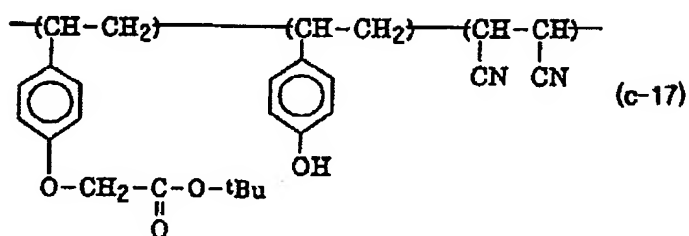
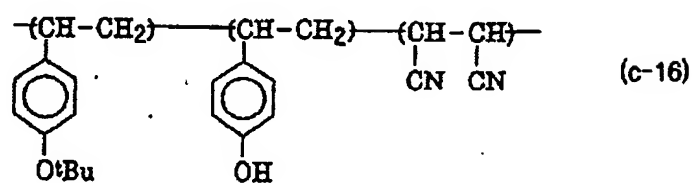


[0144]

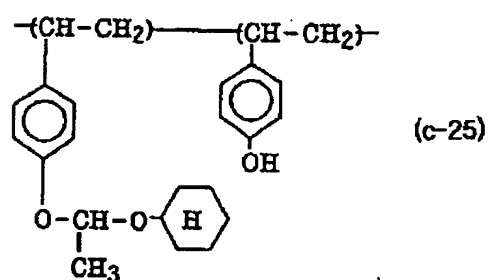
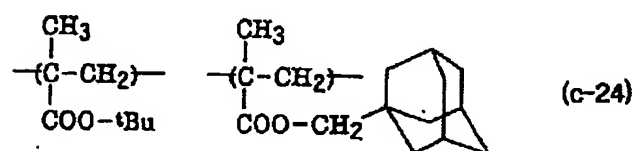
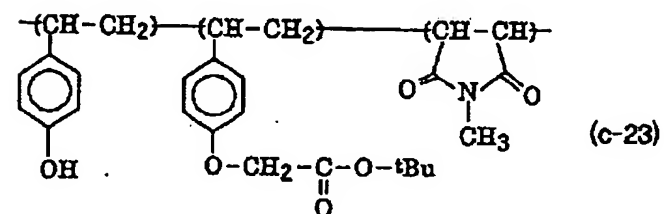
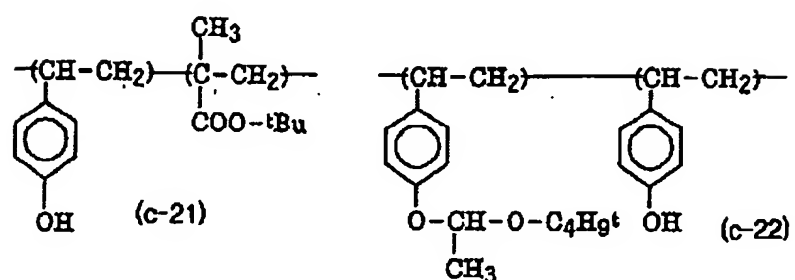
[Formula 57]



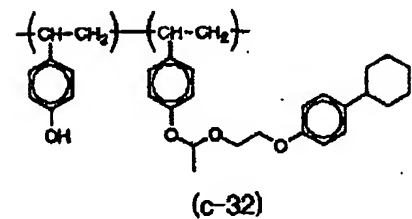
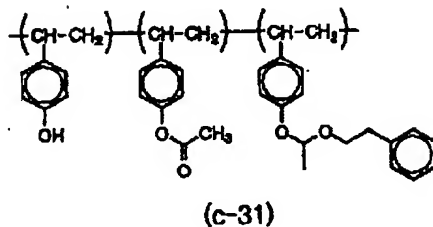
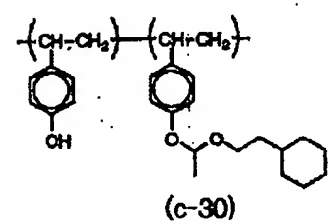
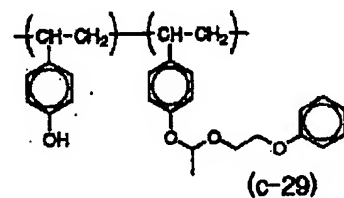
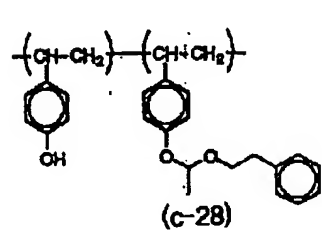
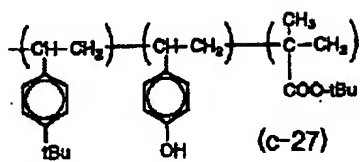
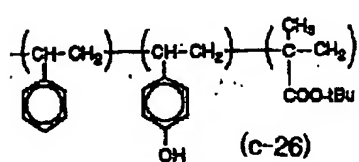
7/11/2006



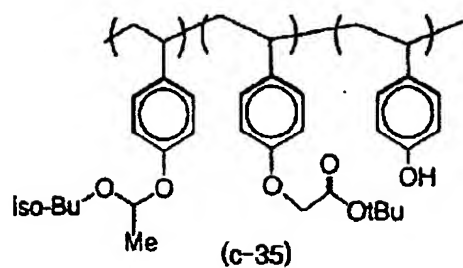
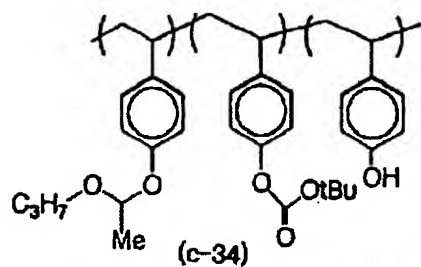
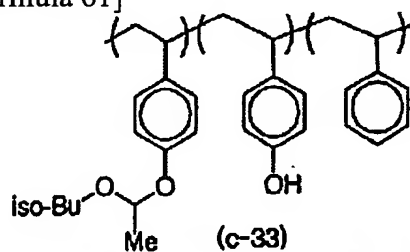
[0146]
[Formula 59]



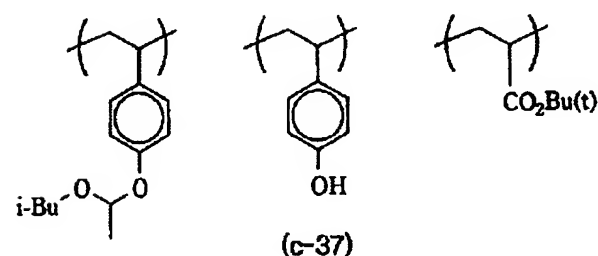
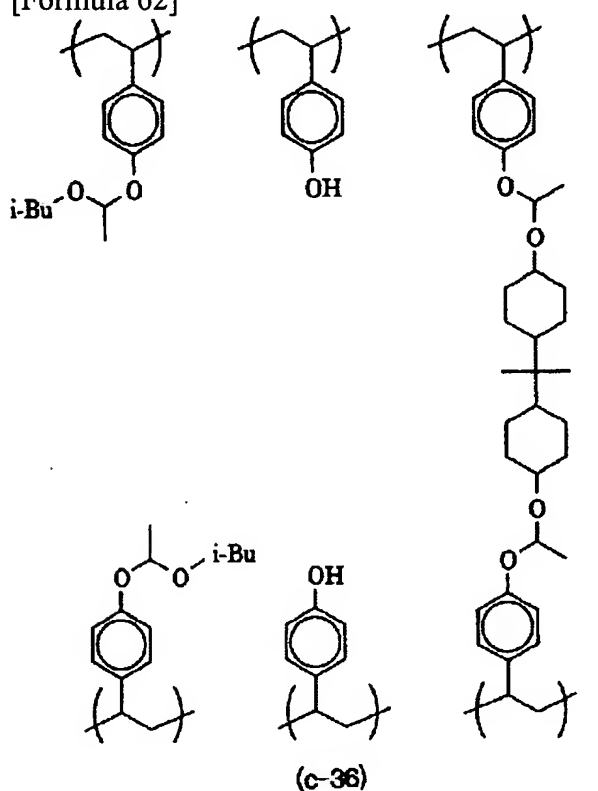
[0147]
[Formula 60]



[0148]
[Formula 61]



[0149]
[Formula 62]



[0150] The content of the radical which may be decomposed from an acid has the number of the radicals which may be decomposed from the acid in resin (B), and the number of the alkali fusibility radicals which are not protected by the radical which may be decomposed from an acid (S), and is expressed with $B/(B+S)$. content -- desirable -- 0.01 to 0.7 -- more -- desirable -- 0.05 to 0.50 -- it is 0.05-0.40 still more preferably. $B/(B+S) >$ It becomes the cause of the film contraction after PEB, the poor adhesion to a substrate, and Society for Cutting Up Men and is not desirable at 0.7. On the other hand, since a standing wave may remain on a pattern side attachment wall notably in $B/(B+S) < 0.01$, it is not desirable.

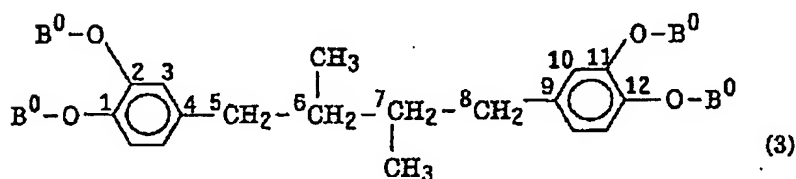
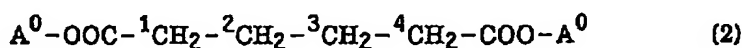
[0151] As for the weight average molecular weight (M_w) of a component (e), it is desirable that it is the range of 2,000-200,000. Less than by 2,000, if film decrease is large and exceeds 200,000 by development of an unexposed part, the dissolution rate to the alkali of alkali fusibility resin itself will become slow, and sensibility will fall. More preferably, it is the range of 5,000-100,000, and is the range of 8,000-50,000 still more preferably. moreover, molecular weight distribution (M_w/M_n) -- desirable -- 1.0-4.0 -- more -- desirable -- 1.0-2.0 -- especially, it is 1.0-1.6 preferably, and thermal resistance and image formation nature (pattern profile etc.) become good, so that degree of dispersion is small. Here, weight average molecular weight has the polystyrene reduced property of gel permeation chromatography, and is defined. Moreover, two or more kinds of components (e) may be used, combining them.

[0152] [IV] (f) low-molecular acidolysis nature lysis inhibition compound "(f) Component"

The (f) component may be used in this invention. (f) A component is a with a molecular weight of 3000 or less low-molecular lysis inhibition compound to which it has the radical which may be decomposed with an acid and the solubility over an alkali developer increases according to an operation of an acid. The desirable (f) component blended with the constituent of this invention is a compound which goes via at least eight joint atoms except an acidolysis nature machine in the location which has at least two radicals which may be decomposed from an acid into the structure, and the distance between these acidolysis nature machines left most. In the location which the more desirable (f) component has at least two radicals which may be decomposed from an acid into the structure, and the distance between these acidolysis nature machines left most In the location from which it has at least ten pieces, the compound via which it goes at least 12 pieces still more preferably, or at least three acidolysis nature machines, and the distance between these acidolysis nature machines separated preferably at least 11 joint atoms except an acidolysis nature machine most They are at least nine pieces and the compound via which it goes at least 11 pieces still more preferably at least ten pieces preferably about the joint atom except an acidolysis nature machine. Moreover, the number of 50 desirable upper limits of the above-mentioned joint atom is 30 still more preferably. (f) When the acidolysis nature lysis inhibition compound which is a component has preferably three or more acidolysis nature machines [four or more], and when separated [beyond a fixed distance that has this acidolysis nature machine mutually] also in what has two acidolysis nature machines, the lysis inhibition nature to alkali fusibility resin improves remarkably. In addition, the distance between acidolysis nature machines is shown by the course joint atomic number except an acidolysis nature machine. For example, in the case of the following compounds (1) and (2), the distance between acidolysis nature machines is four joint atoms respectively, and is 12 joint atoms with a compound (3).

[0153]

[Formula 63]



酸分解性基: $-\text{COO}-\text{A}^0$ 、 $-\text{O}-\text{B}^0$

[0154] Moreover, although the acidolysis nature lysis inhibition compound which is the (f) component may have two or more acidolysis nature machines on the one benzene ring, it is a compound which consists of frames which have one acidolysis nature machine on the one benzene ring preferably. furthermore, the molecular weight of the acidolysis nature lysis inhibition compound of this invention -- 3,000 or less -- it is -- desirable -- 300-3,000 -- it is 500-2,500 still more preferably.

[0155] In the desirable embodiment of this invention, the radical shown by $-\text{R0}-\text{COO}-\text{A0}$ or $-\text{Ar}-\text{O}-\text{B0}$ is mentioned as a radical containing the radical 0 which may be decomposed with an acid, i.e., $-\text{COO}-\text{A}$, and zero $-\text{O}-\text{B}$. A0 shows $-\text{C}$ (R01) (R02) (R03), $-\text{Si}$ (R01) (R02) (R03), or $06-\text{C}$ (R04) (R05)- $\text{O}-\text{R}$ here. B0 shows A0 or zero $-\text{CO}-\text{O}-\text{A}$. Even if R01, R02, R03, R04, and R05 are the same respectively, difference of them may be carried out, a hydrogen atom, an alkyl group, a cycloalkyl radical, an alkenyl radical, or an aryl group is shown, and R06 shows an alkyl group or an aryl group. However, at least two of R01-R03 are radicals other than a hydrogen atom, and two of R01-R03, and R04-R06 radicals may join together, and they may form a ring. R0 shows the aliphatic series or the aromatic hydrocarbon radical more than divalent [which may have the substituent], and $-\text{Ar}-$ shows the aromatic series radical more than divalent [which may have the substituent of a monocycle or many rings].

[0156] As an alkyl group here A methyl group, an ethyl group, a propyl group, n-butyl, The thing of 1-4 carbon

numbers like sec-butyl and t-butyl is desirable. As a cycloalkyl radical, a cyclo propyl group, cyclo butyl, a cyclohexyl radical, The thing of 3-10 carbon numbers like an adamantyl radical is desirable. As an alkenyl radical A vinyl group, The thing of 2-4 carbon numbers like a propenyl radical, an allyl group, and a butenyl group is desirable, and the thing of 6-14 carbon numbers like a phenyl group, a xylyl group, a toluy radical, a KUMENIRU radical, a naphthyl group, and an anthracenyl group as an aryl group is desirable.

[0157] moreover -- as a substituent -- a hydroxyl group and a halogen atom (a fluorine, chlorine, and a bromine --) iodine, a nitro group, a cyano group, the above-mentioned alkyl group, and methoxy group, ethoxy radical, hydroxy ethoxy radical, propoxy group, hydroxy propoxy group, and n-butoxy radical - iso -- alkoxy groups, such as a butoxy radical, a sec-butoxy radical, and a t-butoxy radical, -- Alkoxy carbonyl groups, such as a methoxycarbonyl group and an ethoxycarbonyl radical, Aralkyl radicals, such as benzyl, a phenethyl radical, and a cumyl radical, an aralkyloxy radical, Acyl groups, such as a formyl group, and an acetyl group, a butyryl radical, benzoyl, a SHIANAMIRU radical, a valeryl radical, Alkenyloxy radicals, such as acyloxy radicals, such as a butyryloxy radical, the above-mentioned alkenyl radical, and a vinyloxy radical, a propenyloxy radical, an allyloxy radical, a butenyl oxy-radical, Aryloxy carbonyl groups, such as aryloxy groups, such as the above-mentioned aryl group and a phenoxy group, and a benzoyloxy radical, can be mentioned.

[0158] Preferably, they are a silyl ether group, a cumyl ester group, an acetal radical, a tetrahydropyranyl ether group, an enol ether group, an enol ester group, the alkyl ether radical of the 3rd class, the alkyl ester group of the 3rd class, the alkyl carbonate radical of the 3rd class, etc. Furthermore, they are the 3rd class alkyl ester group, the 3rd class alkyl carbonate radical, a cumyl ester group, and a tetrahydropyranyl ether group preferably.

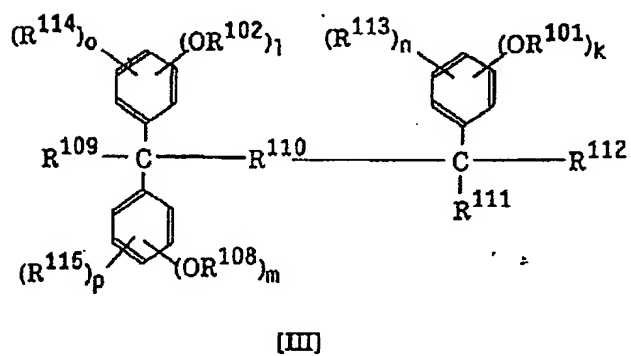
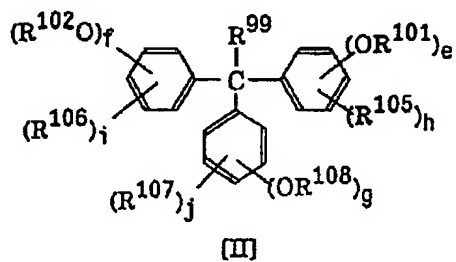
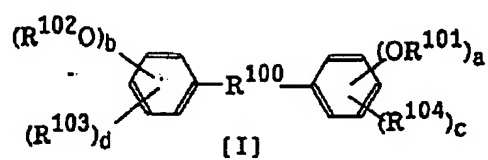
[0159] As a component, preferably (f) JP,1-289946,A, JP,1-289947,A, JP,2-2560,A, JP,3-128959,A, JP,3-158855,A, JP,3-179353,A, JP,3-191351,A, JP,3-200251,A, JP,3-200252,A, JP,3-200253,A, JP,3-200254,A, JP,3-200255,A, JP,3-259149,A, JP,3-279958,A, JP,3-279959,A, JP,4-1650,A, JP,4-1651,A, JP,4-11260,A, JP,4-12356,A, JP,4-12357,A, Japanese Patent Application No. No. 33229 [three to], Japanese Patent Application No. No. 230790 [three to], Japanese Patent Application No. No. 320438 [three to], Japanese Patent Application No. No. 25157 [four to], Japanese Patent Application No. No. 52732 [four to], Japanese Patent Application No. No. 103215 [four to], Japanese Patent Application No. No. 104542 [four to], Japanese Patent Application No. No. 107885 [four to], Japanese Patent Application No. No. 107889 [four to], The compound which combined by the radical which showed above a part or all of a phenol nature OH radical of a polyhydroxy compound that was indicated by specifications, such as 4-152195, -R0-COO-A0, or B0 set, and was protected is contained.

[0160] Preferably Furthermore, JP,1-289946,A, JP,3-128959,A, JP,3-158855,A, JP,3-179353,A, JP,3-200251,A, JP,3-200252,A, JP,3-200255,A, JP,3-259149,A, JP,3-279958,A, JP,4-1650,A, JP,4-11260,A, JP,4-12356,A, JP,4-12357,A, Japanese Patent Application No. No. 25157 [four to], The thing using Japanese Patent Application No. No. 103215 [four to], Japanese Patent Application No. No. 104542 [four to], Japanese Patent Application No. No. 107885 [four to], Japanese Patent Application No. No. 107889 [four to], and the polyhydroxy compound indicated by the specification of 4-152195 is mentioned.

[0161] More specifically, the compound expressed with a general formula [I] - [XVI] is mentioned.

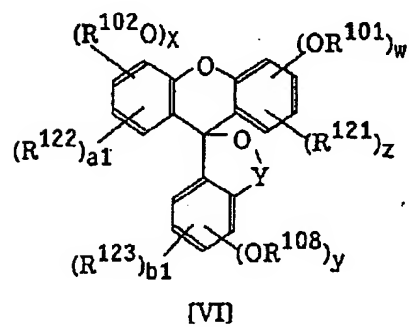
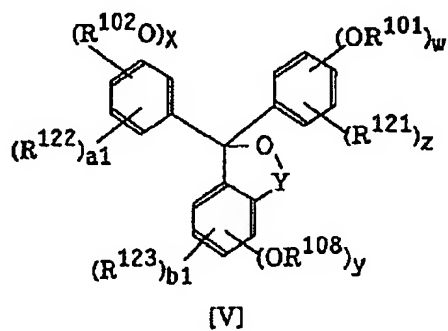
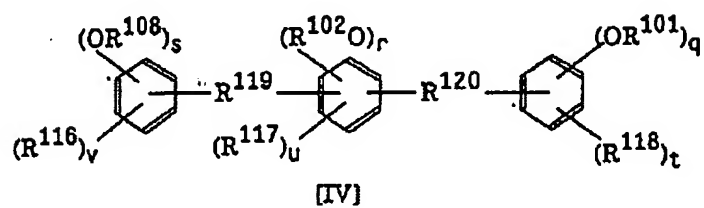
[0162]

[Formula 64]

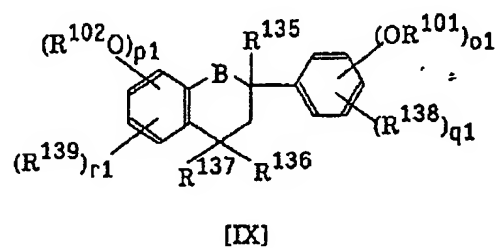
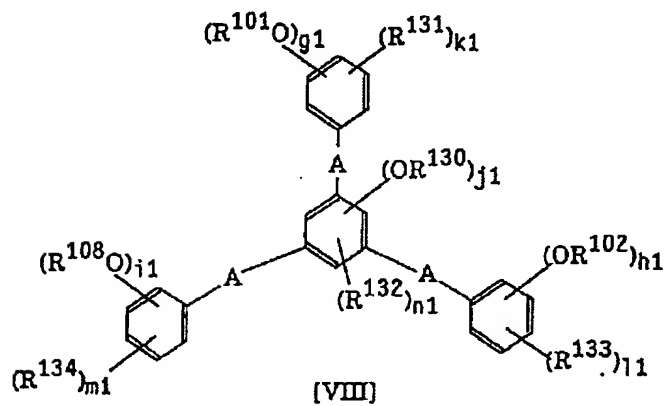
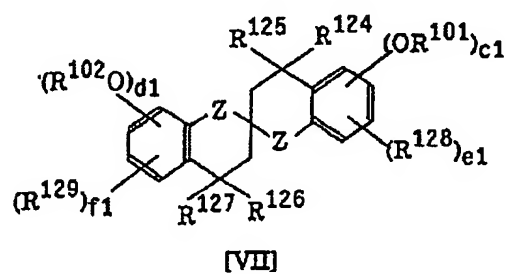


[0163]

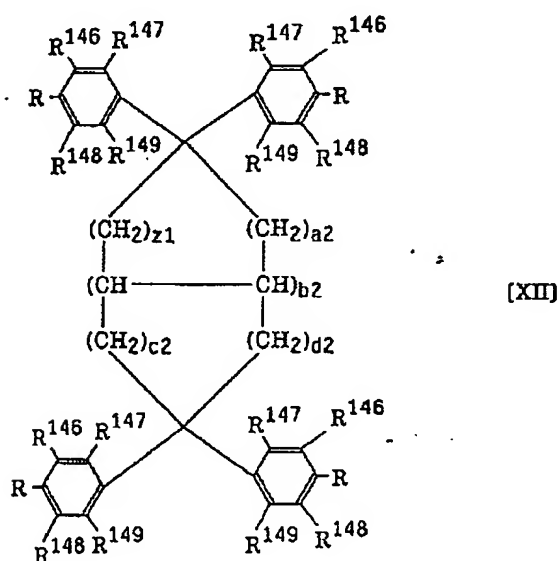
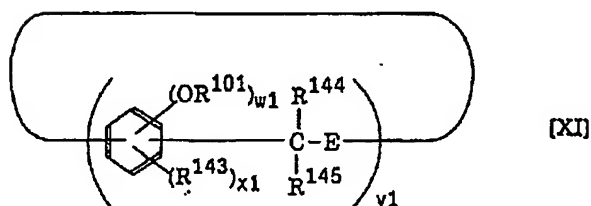
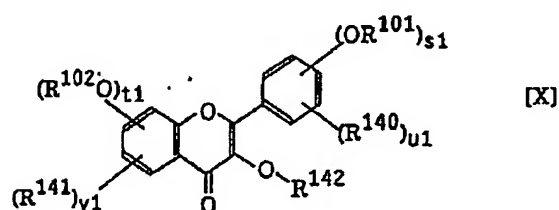
[Formula 65]



[0164]
[Formula 66]



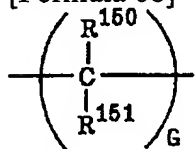
[0165]
[Formula 67]



[0166] Here, it is R¹⁰¹, R¹⁰², R¹⁰⁸, and R¹³⁰. : You may differ, even if the same, and a hydrogen atom, -R⁰-COO-C (R⁰¹) (R⁰²) (R⁰³) or -CO-O-C (R⁰¹) (R⁰²) (R⁰³), however the definition of R⁰, R⁰¹, R⁰², and R⁰³ are the same as the above.

[0167] R¹⁰⁰ : -CO-, -COO-, -NHCONH-, -NHCOO-, -O-, -S-, -SO-, -SO₂-, -SO₃-, or [0168]

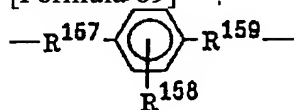
[Formula 68]



[0169] here -- G=2-6 however, the time of G= 2 -- R¹⁵⁰ and R¹⁵¹ inside -- at least one side -- an alkyl group -- R¹⁵⁰, R¹⁵¹ : You may differ, even if the same. A hydrogen atom, an alkyl group, an alkoxy group, - OH, -COOH, -CN, a halogen atom, and -R¹⁵²-COOR¹⁵³ Or -R¹⁵⁴-OH, R¹⁵², R¹⁵⁴ : An alkylene group, R¹⁵³ : A hydrogen atom, an alkyl group, an aryl group, or an aralkyl radical, R⁹⁹, R¹⁰³ -R¹⁰⁷, R¹⁰⁹, and R¹¹¹ -R¹¹⁸, R¹²¹ -R¹²³, R¹²⁸ -R¹²⁹, and R¹³¹ -R¹³⁴, R¹³⁸ -R¹⁴¹ And R¹⁴³ : It may be the same or you may differ. a hydrogen atom, a hydroxyl group, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, an aryloxy group, an aralkyl radical, an aralkyloxy radical, a halogen atom, a nitro group, a carboxyl group, a cyano group, or -N (R¹⁵⁵) (R¹⁵⁶) (here -- R¹⁵⁵ --) R¹⁵⁶ : H, an alkyl group, or aryl group

R110 : Single bond, an alkylene group, or [0170]

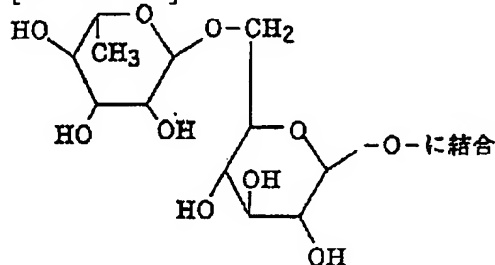
[Formula 69]



[0171] R157, R159 : It may be the same or you may differ. Single bond, an alkylene group, -O-, -S-, -CO-, or a carboxyl group, R158 : A hydrogen atom, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, a nitro group, a hydroxyl group, a cyano group, or a carboxyl group, However, a hydroxyl group may place and replace with an acidolysis nature machine (for example, a t-butoxy carbonylmethyl radical, a tetrahydropyranyl group, a 1-ethoxy-1-ethyl group, a 1-t-butoxy-1-ethyl group).

[0172] R119, R120 : It may be the same or you may differ. A methylene group, a low-grade alkylation methylene group, a halo methylene group, or a halo alkyl group, However, in this application, a low-grade alkyl group points out the alkyl group of carbon numbers 1-4. R124 -R127 : It may be the same or you may differ. A hydrogen atom or an alkyl group, R135 -R137 : It may be the same or you may differ. A hydrogen atom, an alkyl group, an alkoxy group, an acyl group, or an acyloxy radical, R142 : A hydrogen atom, -R0-COO-C (R01) (R02) (R03), -CO-O-C (R01) (R02) (R03), or [0173]

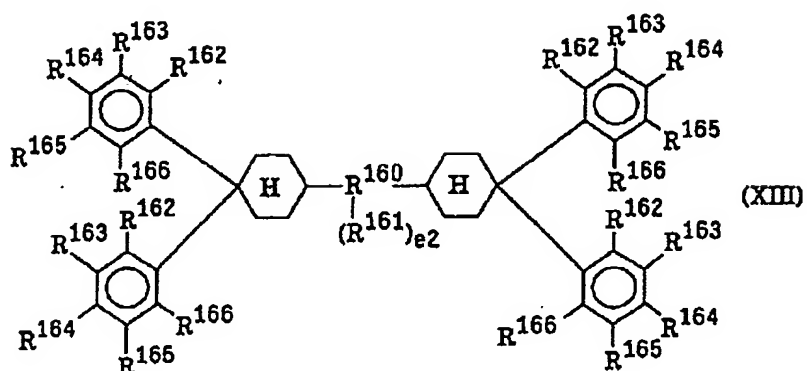
[Formula 70]



[0174] R144, R145 : It may be the same or you may differ. A hydrogen atom, low-grade alkyl group, and low-grade halo alkyl group or an aryl group, R146 -R149 : You may differ, even if the same. A hydrogen atom, a hydroxyl group, a halogen atom, a nitro group, a cyano group, a carbonyl group, an alkyl group, an alkoxy group, an alkoxy carbonyl group, an aralkyl radical, an aralkyloxy radical, an acyl group, an acyloxy radical, an alkenyl radical, an alkenyloxy radical, an aryl group, An aryloxy group or an aryloxy carbonyl group, however the substituent of the four same notations each may not be the same radicals. Y: -CO- or -SO2-, Z, B : Single bond or -O-, A : A methylene group, a low-grade alkylation methylene group, a halo methylene group, or a halo alkyl group, E : At single bond or an oxy-methylene group, a-z, the time of a1-y1:plurality That the radical in () is the same or a-q which may differ, s, t, v, g1-i1, k1-m1, o1, q1, s1 and u1:0, or the integer of 1-5, r, u, wx, y, z, a1-f1, p1, r1, t1, v1-x1:0, or the integer of 1-4, j1, n1, z1, a2, b2, c2, d2:0, or the integer of 1-3, At least one of z1, a2, c2, and d2 1 or more, the integer of y1:3-8, (a+b), (e+f+g), (k+l+m), (q+r+s), (w+x+y), (c1+d1) (g1+h1+i1+j1) (o1+p1) >=(s1+t1) 2, <=(j1+n1) 3, (r+u), (w+z), (x+a1), (y+b1), (c1+e1), (d1+f1), In the case of (p1+r1) (t1+v1) <=(x1+w1) 4, however a general formula [V], (w+z), (x+a1) <=5 and (a+c) (b+d) (e+h) (f+i) (g+j) (k+n) (l+o) (m+p) (q+t) (second+v) (g1+k1) (h1+l1) (i1+m1) (o1+q1) <=(s1+u1) 5 are expressed.

[0175]

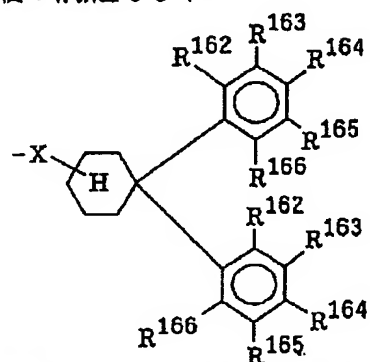
[Formula 71]



ここで、

R^{160} : 有機基、単結合、 $-S-$ 、 $-SO-$ もしくは $-\overset{\text{O}}{\parallel}\text{S}-\overset{\text{O}}{\parallel}$

R^{161} : 水素原子、一価の有機基もしくは



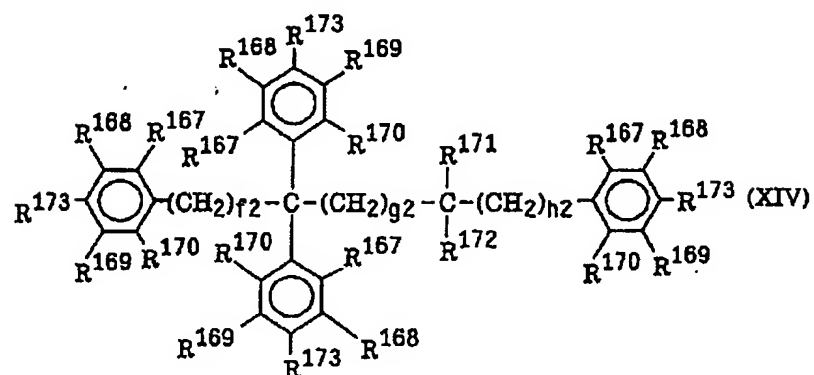
$R^{162} \sim R^{166}$: 同一でも異なっても良く、水素原子、水酸基、ハロゲン原子、アルキル基、アルコキシ基、アルケニル基、 $-O-R^0-COO-C(R^{01})(R^{02})(R^{03})$ もしくは $-O-CO-O-C(R^{01})(R^{02})(R^{03})$ 、但し、少なくとも2つは $-O-R^0-COO-C(R^{01})(R^{02})(R^{03})$ もしくは $-O-CO-O-C(R^{01})(R^{02})(R^{03})$ である；又、各4もしくは6個の同一記号の置換基は同一の基でなくても良い、

X : 2価の有機基、

$e2$: 0もしくは1、を表わす。

[0176]

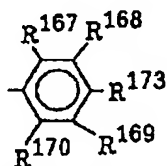
[Formula 72]



ここで、

$R^{167} \sim R^{170}$: 同一でも異なっても良く、水素原子、水酸基、ハロゲン原子、アルキル基、アルコキシ基、もしくはアルケニル基、但し、各4~6個の同一記号の置換基は同一の基でなくても良い、

R^{171}, R^{172} : 水素原子、アルキル基もしくは



R^{173} : 少なくとも2つは $-O-R^0-COO-C(R^{01})(R^{02})(R^{03})$ 基もしくは $-O-CO-O-C(R^{01})(R^{02})(R^{03})$ 基であり、その他は水酸基である、

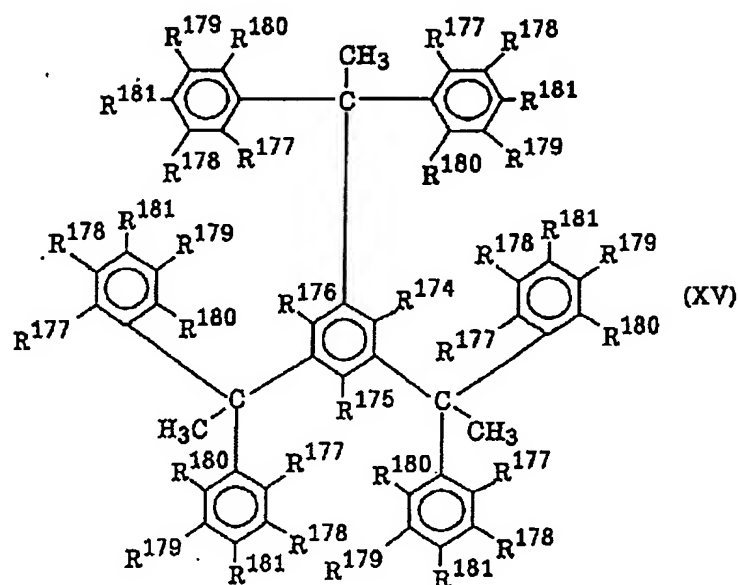
$f2, h2$: 0もしくは1、

$g2$: 0もしくは1~4の整数、

を表す。

[0177]

[Formula 73]



ここで、

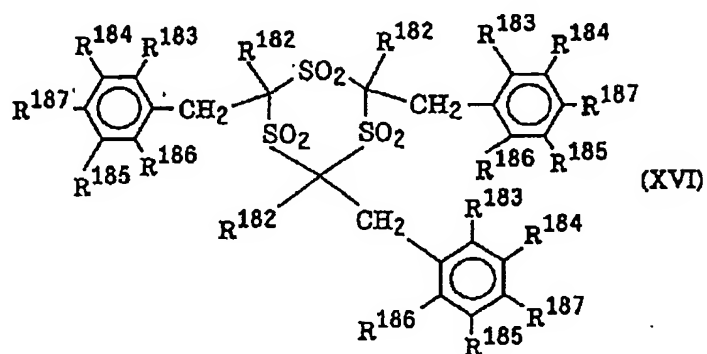
$R^{174} \sim R^{180}$: 同一でも異なっても良く、水素原子、水酸基、ハロゲン原子、アルキル基、アルコキシ基、ニトロ基、アルケニル基、アリール基、アラルキル基、アルコキシカルボニル基、アリールカルボニル基、アシロキシ基、アシル基、アラルキルオキシ基もしくはアリールオキシ基、但し、各6個の同一記号の置換基は同一の基でなくても良い、

R^{181} : 少なくとも2つは $-O-R^0-COO-C(R^{01})(R^{02})(R^{03})$ 基もしくは $-O-CO-O-C(R^{01})(R^{02})(R^{03})$ 基であり、その他は水酸基である、

を表す。

[0178]

[Formula 74]



ここで、

R^{182} : 水素原子もしくはアルキル基、但し、全部同一でなくとも良い、

$R^{183} \sim R^{186}$: 水酸基、水素原子、ハロゲン原子、アルキル基、もしくはアルコキシ基、但し、各3個の同一記号の置換基は同一の基でなくとも良い、

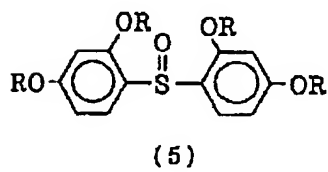
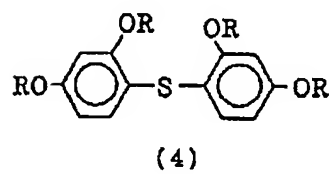
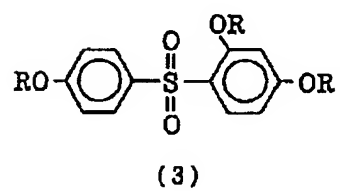
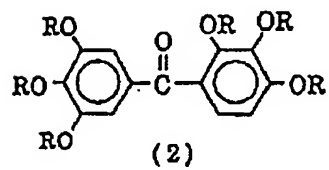
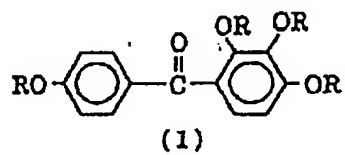
R^{187} : 少なくとも2つは $-O-R^0-COO-C(R^{01})(R^{02})(R^{03})$ 基もしくは、 $-O-CO-O-C(R^{01})(R^{02})(R^{03})$ 基であり、その他は水酸基である、

を表す。

[0179] The example of a desirable compound frame is shown below.

[0180]

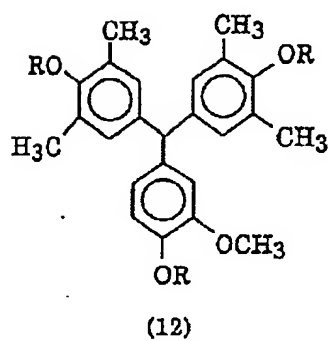
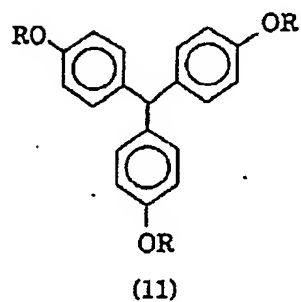
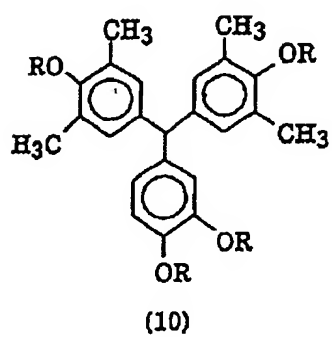
[Formula 75]



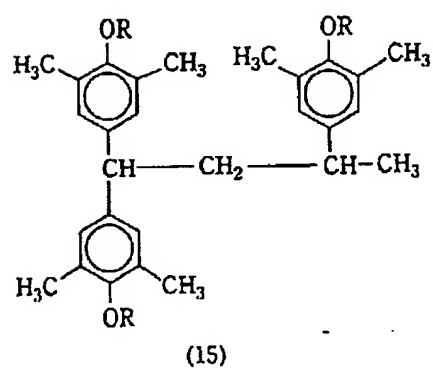
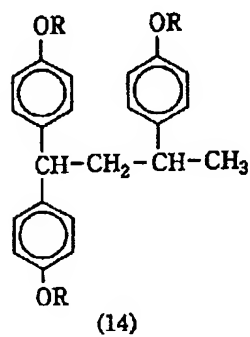
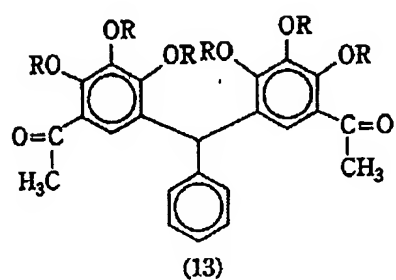
[0181]
[Formula 76]



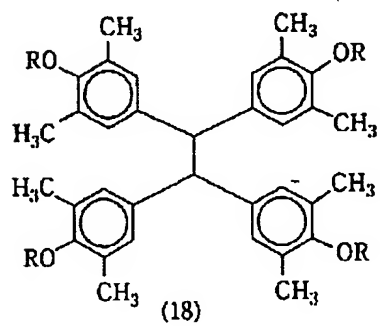
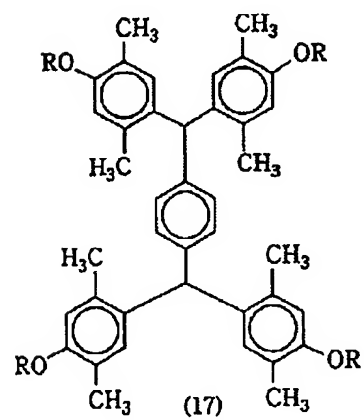
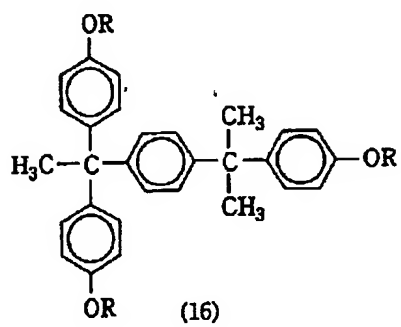
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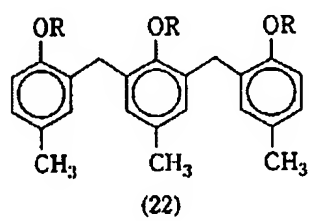
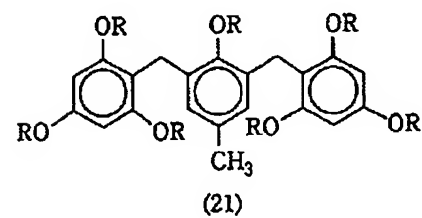
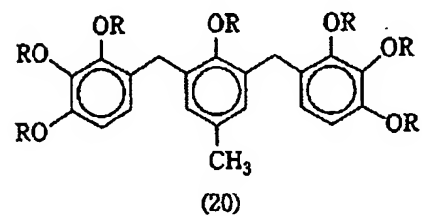
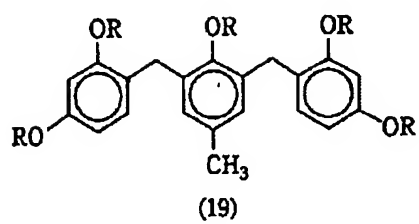
[0183]
[Formula 78]



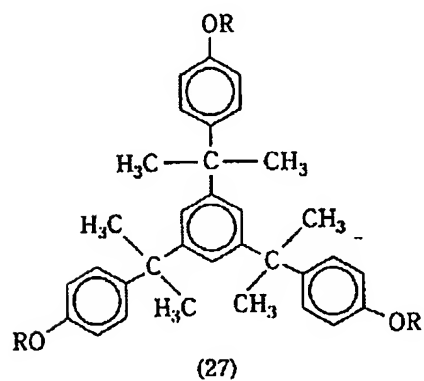
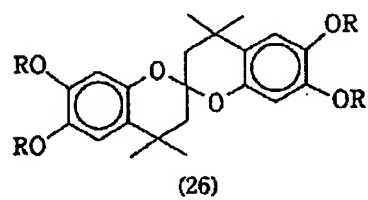
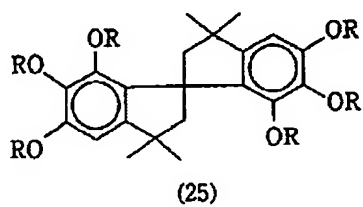
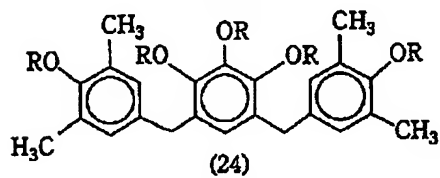
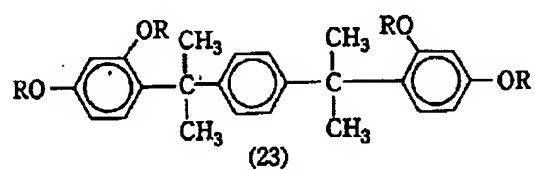
[0184]
[Formula 79]



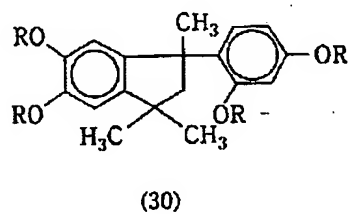
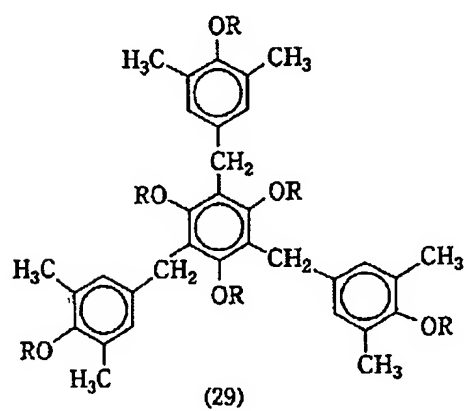
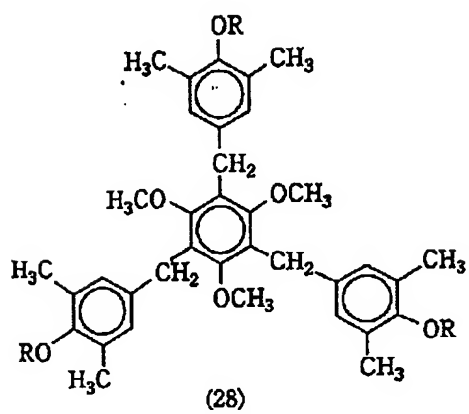
[0185]
[Formula 80]



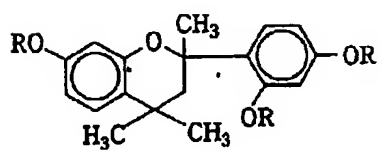
[0186]
[Formula 81]



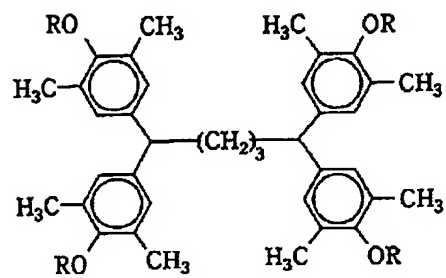
[0187]
[Formula 82]



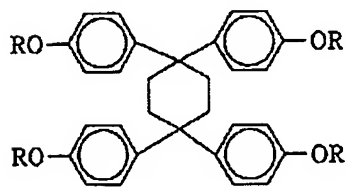
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[Formula 83]



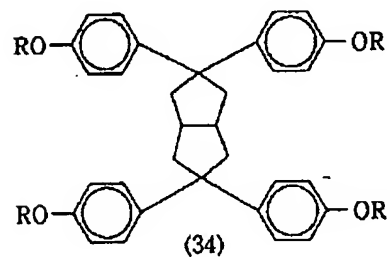
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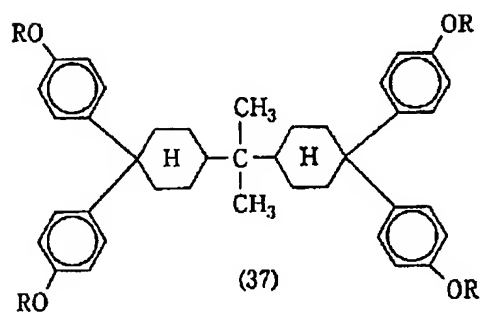
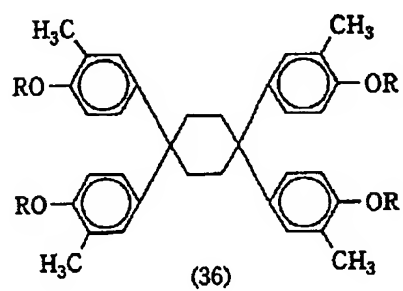
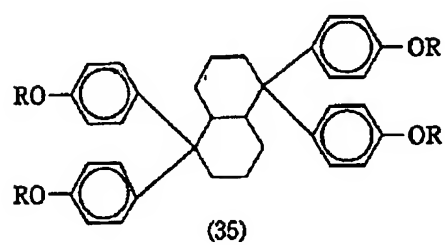
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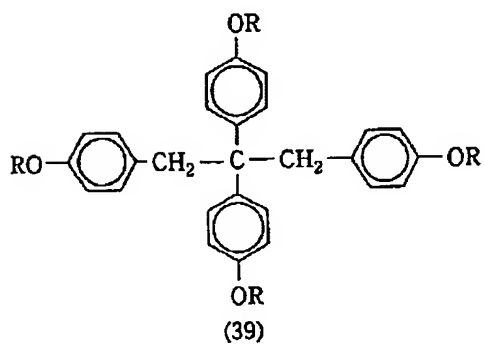
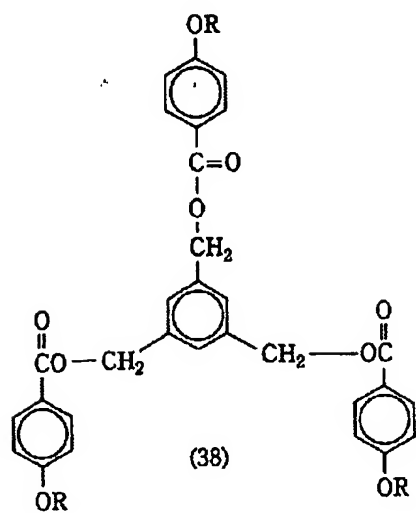
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[0189]

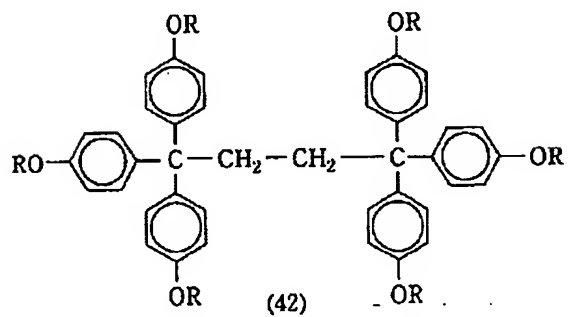
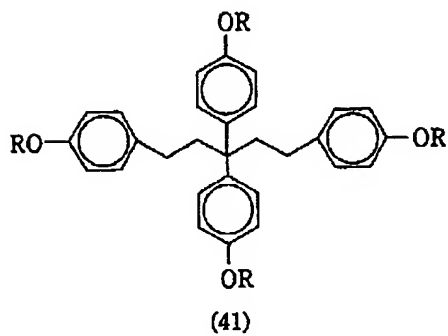
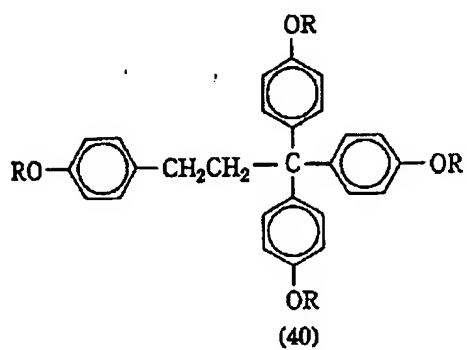
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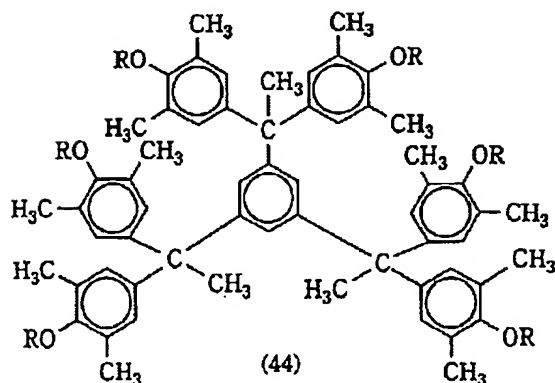
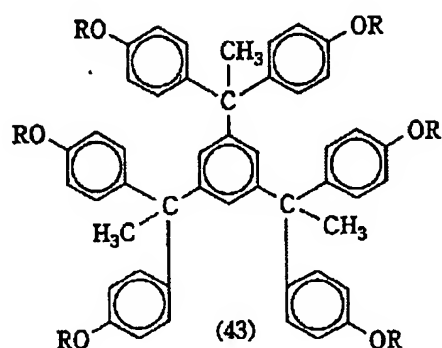
[0190]
[Formula 85]



[0191]
[Formula 86]

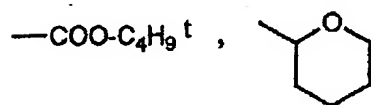


[0192]
[Formula 87]



[0193] R in compound (1) - (44) is a hydrogen atom and [0194].

[Formula 88]



[0195] ***** However, three pieces may be radicals other than a hydrogen atom by at least two pieces or structure, and each substituent R may not be the same radical.

[0196] [V] As other components, it is insoluble in (g) water and meltable resin (henceforth "(g) component" or "(g) alkali fusibility resin") can be used for this invention at an alkali developer. In the positive type chemistry magnification resist constituent of this invention, as a (g) component, it is insoluble in water and meltable resin can be used for an alkali water solution. (g) When using a component, an operation of the acid which is the above-mentioned (g) component decomposes, and there is not necessarily no need of blending the resin which has the radical which increases the solubility in the inside of an alkali developer. Of course, concomitant use with the (g) component is not eliminated.

[0197] As (g) alkali fusibility resin used for this invention For example, novolak resin, hydrogenation novolak resin, acetone-pyrogallol resin, o-polyhydroxy styrene, m-polyhydroxy styrene, p-polyhydroxy styrene, Hydrogenation polyhydroxy styrene, a halogen, or alkylation polyhydroxy styrene, A hydroxystyrene-N-permutation maleimide copolymer, o/p-, and a m/p-hydroxystyrene copolymer, the part to the hydroxyl group of polyhydroxy styrene -- O-alkylation object for example, 5-30-mol % O-methylation object and O-(1-methoxy) ethylation object -- O-(1-ethoxy) ethylation object, an O-2-tetrahydropyranyl ghost, O-acylation objects, such as O-(t-butoxycarbonyl) methylation object For example, (5 - 30-mol % o-acetylation object, O-(t-butoxy) carbonylation object), etc., Although a styrene maleic anhydride copolymer, a styrene-hydroxystyrene copolymer, an alpha-methyl-styrene-hydroxystyrene copolymer, carboxyl group content methacrylic system resin and its derivative, and a polyvinyl alcohol derivative can be mentioned It is not limited to these.

[0198] especially desirable (g) alkali fusibility resin -- a part of novolak resin and o-polyhydroxy styrene, m-polyhydroxy styrene, p-polyhydroxy styrene and these copolymer, alkylation polyhydroxy styrene, and polyhydroxy styrene -- they are O-alkylation or O-acylation object, a styrene-hydroxystyrene copolymer, and an alpha-methylstyrene-hydroxystyrene copolymer. This novolak resin is obtained by carrying out addition condensation to aldehydes under existence of an acid catalyst by using a predetermined monomer as a principal component.

[0199] As a predetermined monomer, a phenol, m-cresol, p-cresol, Cresol, such as o-cresol, 2, 5-xylenol, 3,5-xylenol, Xylenols, such as 3, 4-xylenol, 2, and 3-xylenol m-ethylphenol, p-ethylphenol, o-ethylphenol, Alkylphenols, such as p-t-butylphenol, p-octyl phenol, 2 and 3, and a 5-trimethyl phenol p-methoxy phenol, m-methoxy phenol, 3, 5-dimethoxy phenol, 2-methoxy-4-methyl phenol, an m-ethoxy phenol, a p-ethoxy phenol, An m-propoxy phenol, a p-propoxy phenol, an m-butoxy phenol, Bis-alkylphenols, such as alkoxy phenols, such as a p-butoxy phenol, and a 2-methyl-4-isopropyl phenol independent in hydroxy aroma compounds, such as m-chlorophenol, p-chlorophenol, o-chlorophenol, a dihydroxy biphenyl, bisphenol A, phenylphenol, resorcinol, and a naphthol, -- or, although two or more kinds can use it, mixing It is not limited to these.

[0200] As aldehydes, for example Formaldehyde, a paraformaldehyde, An acetaldehyde, propionaldehyde, a benzaldehyde, phenylacetaldehyde, alpha-phenylpropyl aldehyde, beta-phenylpropyl aldehyde, Ortho hydroxybenzaldehyde, an m-hydroxy benzaldehyde, A p-hydroxy benzaldehyde, o-chlorobenzaldehyde, m-chlorobenzaldehyde, p-chlorobenzaldehyde, o-nitro benzaldehyde, m-nitro benzaldehyde, p-nitro benzaldehyde, o-methyl benzaldehyde, m-methyl benzaldehyde, Although p-methyl benzaldehyde, p-ethyl benzaldehyde, a p-n-butyl benzaldehyde, a furfural, chloroacetaldehyde, and these acetal objects, for example, a chloroacetaldehyde diethyl acetal etc., can be used In these, it is desirable to use formaldehyde. These aldehydes are independent, or they are combined two or more kinds and used. As an acid catalyst, a hydrochloric acid, a sulfuric acid, a formic acid, an acetic acid, oxalic acid, etc. can be used.

[0201] In this way, as for the weight average molecular weight of the obtained novolak resin, it is desirable that it is the range of 1,000-30,000. Less than by 1,000, if the film decrease after the development of an unexposed part is large and exceeds 30,000, a development rate will become small. The range especially of a suitable thing is 2,000-20,000. moreover, the weight average molecular weight of said polyhydroxy styrene other than novolak resin and its derivative, and a copolymer -- 2000 or more -- desirable -- 5000-200000 -- it is 5000-100000 more preferably. Here, weight average molecular weight has the polystyrene reduced property of gel permeation chromatography, and is defined. It may be used combining two or more kinds of these (g) alkali fusibility resin in this invention.

[0202] Here, the example of a configuration of the constituent of this invention is illustrated below. However, the contents of this invention are not limited to these.

- 1) The positive type chemistry magnification resist constituent containing the above-mentioned component (a), the above-mentioned component (b), the above-mentioned component (c), and the above-mentioned component (e).
- 2) The positive type chemistry magnification resist constituent containing the above-mentioned component (a), the above-mentioned component (b), the above-mentioned component (c), the above-mentioned component (f), and said component (g).
- 3) The positive type chemistry magnification resist constituent containing the above-mentioned component (a), the above-mentioned component (b), the above-mentioned component (c), the above-mentioned component (e), and the above-mentioned component (f).

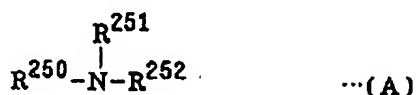
[0203] In each above-mentioned example of a configuration, respectively, the amount of [in / used / the constituent of the component (e) of 1, the component (g) of 2, and the component (e) of 3] has 40 - 99 desirable % of the weight to the solid content of all constituents, and is 50 - 95 % of the weight more preferably.

[0204] the amount of [in / used / the constituent of said component (f)] -- each above-mentioned example of a configuration -- either has 3 - 45 desirable % of the weight to the solid content of all constituents, and is 10 - 30 % of the weight still more preferably five to 30% of the weight more preferably.

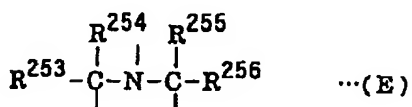
[0205] [VI] (c) organic base nature compound used by (c) organic base nature compound this invention is a compound with basicity stronger than a phenol. A nitrogen-containing basicity compound is desirable especially. As desirable chemical environment, following (type A) - (E) structure can be mentioned.

[0206]

[Formula 89]



ここで、 R^{250} 、 R^{251} および R^{252} は、同一または異なり、水素原子、炭素数1~6のアルキル基、炭素数1~6のアミノアルキル基、炭素数1~6のヒドロキシアルキル基または炭素数6~20の置換もしくは非置換のアリール基であり、ここで R^{251} と R^{252} は互いに結合して環を形成してもよい。



(式中、 R^{253} 、 R^{254} 、 R^{255} および R^{256} は、同一または異なり、炭素数1~6のアルキル基を示す)

[0207] Furthermore, a desirable compound is a nitrogen-containing basicity compound which has two or more nitrogen atoms of different chemical environment in a monad, and is a compound which has especially a compound or alkylamino radical including both ring structures containing the amino group and nitrogen atom which are not permuted [a permutation or] preferably. As a desirable example, the aminopyridine which is not permuted [the guanidine which is not permuted / a permutation or / a permutation, or], The amino pyrrolidine which is not permuted [the amino alkyl pyridine which is not permuted / a permutation or / a permutation, or], The pyrazole which is not permuted [in DAZORU which is not permuted / a permutation or /, a permutation or], The pyrimidine which is not permuted [the pyrazine which is not permuted / a permutation or /, a permutation, or], The amino alkyl morpholine which is not permuted [the amino morpholine which is not permuted / the piperazine which is not permuted / the pyrazoline which is not permuted / the imidazoline which is not permuted / the pudding which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or] is mentioned. Desirable substituents are the amino group, an amino alkyl group, an alkylamino radical, an amino aryl group, an arylamino radical, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, an aryloxy group, a nitro group, a hydroxyl group, and a cyano group.

[0208] As a desirable compound, especially Guanidine, 1, and 1-dimethyl guanidine, 1, 1, 3, 3, - tetramethyl guanidine, an imidazole, 2-methylimidazole, 4-methyl imidazole, N-methyl imidazole, 2-phenylimidazole, 4, 5-diphenyl imidazole, 2 and 4, 5-triphenyl imidazole, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylamino pyridine, 4-dimethylaminopyridine, 2-diethylamino pyridine, 2-(aminomethyl) pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethyl pyridine, 4-aminoethyl pyridine, 3-amino pyrrolidine, A piperazine, N-(2-aminoethyl) piperazine, N-(2-aminoethyl) piperidine, 4-amino - 2, 2, 6, and 6-tetramethylpiperidine, 4-piperidino piperidine, A 2-imino piperidine, 1-(2-aminoethyl) pyrrolidine, a pyrazole, 3-amino-5-methyl pyrazole, 5 - Amino-3-methyl-1-p-tolyl pyrazole, Pyrazine, 2-(aminomethyl)-5-methyl pyrazine, a pyrimidine, 2, 4-diamino pyrimidine, 4, 6-dihydroxy pyrimidine, 2-pyrazoline, Although 3-pyrazoline, N-amino morpholine, N-(2-aminoethyl) morpholine, diazabicyclo nonene, diazabicycloudecen, etc. are mentioned, it is not

limited to this.

[0209] these (c) organic base nature compounds are independent -- it is -- two or more sorts can be combined and it can use. the compound to which the amount of the organic base nature compound used generates an acid by the exposure of the (a) radiation of this invention -- receiving -- usually -- 0.01 - ten-mol % -- it is 0.1 - five-mol % preferably. Less than [0.01 mol %], the effectiveness of the addition is not acquired. On the other hand, when ten-mol % is exceeded, there is an inclination for the development nature of the fall of sensibility or a non-exposed area to get worse.

[0210] [VII] (d) fluorine system and/or a silicon system surfactant can be used for (d) fluorine system and/or silicon system surfactant this invention. For example, a fluorochemical surfactant or silicon system surfactants, such as EFUTOPPU EF301 and EF303 (new Akita formation Make), Fluorad 430 and FC 431 (Sumitomo 3M make), the megger fucks F171, F173, F176, F189, and R08 (Dainippon Ink make), Sir chlorofluocarbon S-382, SC-101, 102, 103, 104, 105 and 106 (Asahi Glass Co., Ltd. make), and Troysol S-366 (made in Troy Chemical), can be mentioned. Moreover, polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make) can be used as a silicon system surfactant.

[0211] Surfactants other than a fluorine system and/or a silicon system surfactant can also be used together. Specifically The polyoxyethylene lauryl ether, polyoxyethylene stearylether, Polyoxyethylene alkyl ether, such as the polyoxyethylene cetyl ether and the polyoxyethylene oleyl ether Polyoxyethylene alkyl aryl ether, such as the polyoxyethylene octyl phenol ether and the polyoxyethylene nonyl phenol ether Polyoxyethylene polyoxypropylene block copolymers Sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, Sorbitan fatty acid esters, such as sorbitan monooleate, sorbitan trioleate, and sorbitan tristearate Polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, Polyoxyethylenesorbitan monostearate, polyoxyethylene sorbitan trioleate, The Nonion system surfactants, such as polyoxyethylene sorbitan fatty acid ester, such as polyoxyethylene sorbitan tristearate, An acrylic-acid system or methacrylic-acid system (**) polymerization poly flow No.75, No.95 (product made from Kyoeisha Fats-and-oils Chemical industry), etc. can be mentioned.

[0212] The loadings of these surfactants are usually 1 or less % of the weight preferably 2 or less % of the weight to the solid content of all the constituents in the constituent of this invention. You may add independently and these surfactants can also be added combining two or more sorts.

[0213] [VIII] The positive type chemistry magnification resist constituent of component this invention of others which are used for this invention can be made to contain the compound which has two or more phenol nature OH radicals which promote the solubility over a color, a pigment, a plasticizer, a photosensitizer, and a developer further if needed.

[0214] The compound which has two or more phenol nature OH radicals which can be used by this invention is a with a molecular weight of 1000 or less phenolic compound preferably. Moreover, although it is required in a molecule to have at least two phenolic hydroxyl groups, if this exceeds 10, the amelioration effectiveness of development latitude will be lost. Moreover, the ratio of a phenolic hydroxyl group and a ring has a large thickness dependency at less than 0.5, and there is an inclination for development latitude to become narrow. It becomes difficult and is not desirable for the stability of this constituent to deteriorate, if this ratio exceeds 1.4, and to acquire a high resolution and good thickness dependency.

[0215] The desirable addition of this phenolic compound is 2 - 50 % of the weight to (g) alkali fusibility resin, and is 5 - 30 % of the weight still more preferably. The new fault that development residue gets worse and a pattern deforms in the addition exceeding 50 % of the weight at the time of development generates and is not desirable.

[0216] Such a with a molecular weight of 1000 or less phenolic compound can refer to an approach given in JP,4-122938,A, JP,2-28531,A, United States patent 4916210th, and the Europe patent 219294th grade, and can compound it easily in this contractor. Although the example of a phenolic compound is shown below, the compound which can be used by this invention is not limited to these.

[0217] Resorcinol, phloroglucine, 2 and 3, 4-trihydroxy benzophenone, A 2, 3, 4, and 4'-tetra-hydroxy benzophenone, 2, 3 and 4, 3', 4', and 5'-hexa hydroxy benzophenone, Acetone-pyrogallol condensation resin, FURORO glucoside, 2 and 4, 2', and 4'-biphenyl tetrol, 4,4'-thiobis (1, 3-dihydroxy) benzene, 2, 2', 4, and 4'-tetra-hydroxy diphenyl ether, 2, 2', 4, and 4'-tetra-hydroxy diphenyl sulfoxide, 2, 2', 4, and 4'-tetra-hydroxy diphenyl sulfone, tris (4-hydroxyphenyl) methane, 1 and 1-bis(4-hydroxyphenyl) cyclohexane, 4, and 4-(alpha-methyl benzylidene) bisphenol, alpha, alpha', alpha"-tris (4-hydroxyphenyl) - 1, 3, 5-triisopropyl benzene, alpha, alpha', alpha"-tris (4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene, 1, 2, and 2-tris (hydroxyphenyl) propane, 1 and 1, 2-tris (3, 5-dimethyl-4-hydroxyphenyl) propane, 2, 2, 5, and 5-tetrakis (4-hydroxyphenyl) hexane, 1, 2-tetrakis (4-hydroxyphenyl) ethane, 1 and 1, 3-tris

(hydroxyphenyl) butane, a Para [α , α , α' , and α' -tetrakis (4-hydroxyphenyl)]-xylene, etc. can be mentioned.

[0218] The constituent of this invention is melted to the solvent which dissolves each above-mentioned component, and is applied on a base material. As a solvent used here, ethylene dichloride, a cyclohexanone, Cyclopentanone, 2-heptanone, gamma-butyrolactone, a methyl ethyl ketone, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxy ethyl acetate, ethylene glycol monoethyl ether acetate, Propylene glycol monomethyl ether, propylene-glycol-monomethyl-ether acetate, Propylene-glycol-monomethyl-ether propionate, toluene, Ethyl acetate, methyl lactate, ethyl lactate, methoxy methyl propionate, Ethoxy ethyl propionate, methyl pyruvate, pyruvic-acid ethyl, pyruvic-acid propyl, N,N-dimethylformamide, dimethyl sulfoxide, N-methyl pyrrolidone, a tetrahydrofuran, etc. are desirable, and independent in these solvents -- or it can be mixed and used. In this invention, especially as a spreading solvent, propylene-glycol-monomethyl-ether acetate is desirable, and, thereby, excellent in the homogeneity within a field. [come]

[0219] In addition to engine performance, such as high resolution of an essential resist, pursuit of the further advance of a semi-conductor demands the constituent of high performance from various viewpoints, such as sensibility, spreading nature, the minimum spreading initial complement, adhesion with a substrate, thermal resistance, and the preservation stability of a constituent. Recently, in order to increase the absolute magnitude which can take the chip of completion, it is in the inclination which creates a device using Wafer of the diameter of macrostomia. However, if it applies to the diameter of macrostomia, in order to be anxious about the fall of thickness homogeneity within spreading nature, especially a field, the improvement in the homogeneity within the thickness side to Wafer of the diameter of macrostomia is demanded. Thickness measurement can be performed at the a large number point in Wafer as the technique of the ability to check this homogeneity, the standard deviation of each measured value can be taken, and homogeneity can be checked by one 3 times that value of this. It can be said that the homogeneity within a field is high, so that this value is small. As a value, the one of 100 or less 3 times the value of standard deviation is desirable, and 50 or less are more desirable. Moreover, also in the mask manufacture for optical lithography, importance is maximum-attached to CD linearity, and the improvement in the homogeneity within the thickness side in BURANKUSU is demanded.

[0220] The resist constituent of this invention can be filtered after melting to a solvent. Therefore, although the filter used is used in the resist field, it is chosen from inside, and that in which the quality of the material of a filter contains polyethylene, nylon, or polysulfone is specifically used. More specifically, they are the micro guard by Millipore Corp., the micro guard Plus, micro guard MINIKEMU-D, and micro guard MINIKEMU-D. PR, Millipore OBUCHI mizer DEV/DEV-C, Millipore The OBUCHI mizers 16/14, URUCHIBOA N66 by the pole company, POJIDAIN, a nylon falcon, etc. are mentioned. Moreover, what was checked by the following approach can be used about the aperture of a filter. That is, a PSL standard particle (polystyrene latex bead particle diameter of 0.100 micrometers) is distributed in ultrapure water, with a tube pump, continuously, a sink and challenge concentration are measured with a particle counter in the amount of steady flow, and what has been caught 90% or more can be used for a primary filter side as a 0.1 micrometer filter of apertures.

[0221] The positive type chemistry magnification resist constituent of this invention can be exposed through a predetermined mask after spreading by the suitable methods of application, such as a spinner and a coating machine, on a substrate (example: silicon / diacid-ized silicon covering) which is used for manufacture of a precision integrated circuit device, or the substrate for mask manufacture for optical lithography (example: glass / Cr covering), and a good resist pattern can be obtained by developing negatives by performing BEKU.

[0222] As a developer of the constituent of this invention, a sodium hydroxide, a potassium hydroxide, Inorganic alkali, such as a sodium carbonate, a sodium silicate, a meta-sodium silicate, and aqueous ammonia Primary amines, such as ethylamine and n propylamine, diethylamine, Tertiary amines, such as secondary amines, such as G n butylamine, triethylamine, and methyl diethylamine Alcoholic amines, such as dimethylethanolamine and triethanolamine, Alkaline water solutions, such as annular amines, such as quarternary ammonium salt, such as tetramethylammonium hydroxide and tetraethylammonium hydroxide, a pyrrole, and a piperidine, can be used. Furthermore, alcohols and a surfactant can also be used for the alkaline above-mentioned water solution, carrying out suitable amount addition.

[0223]

[Example] Hereafter, although an example explains this invention to a detail further, thereby, the contents of this invention are not limited.

[Composition of a synthetic example 1:Pori (p-hydroxystyrene / styrene) copolymer] It was based on the conventional method, and it dehydrated and p-tert-butoxy styrene monomer 35.25g (0.2 mols) and styrene monomer 5.21g (0.05 mols) which carried out distillation purification were dissolved in tetrahydrofuran 100ml. The polymerization reaction was performed by adding azobisisobutyronitril (azobisisobutironitoriru) 0.033g 3 times every 2.5 hours at 80 degrees C under a nitrogen air current and stirring, and finally continuing stirring for further 5 hours. Reaction mixture was supplied to hexane 1200ml, and white resin was deposited. It dissolved in tetrahydrofuran 150ml after drying the obtained resin. After adding 4-N hydrochloric acid to this and making it hydrolyze by carrying out heating reflux for 6 hours, it reprecipitates to the ultrapure water of 5L, and this resin was carried out the ** exception, and was rinsed and dried. Furthermore, it dissolved in tetrahydrofuran 200ml, and dropping and reprecipitation were performed, stirring violently in the ultrapure water of 5L. This reprecipitation actuation was repeated 3 times. 120 degrees C of obtained resin were dried in the vacuum desiccator for 12 hours, and the Pori (p-hydroxystyrene / styrene) copolymer was obtained.

[0224] [Composition of the example of synthetic example 2:resin (c-21)] The polymerization reaction was performed by dissolving p-acetoxy styrene 32.4g (0.2 mols) and 7.01g (0.07 mols) of t-butyl methacrylate in 120ml of butyl acetate, adding azobisisobutyronitril (azobisisobutironitoriru) 0.033g 3 times every 2.5 hours at 80 degrees C under a nitrogen air current and stirring, and finally continuing stirring for further 5 hours. Reaction mixture was supplied to hexane 1200ml, and white resin was deposited. It dissolved in methanol 200ml after drying the obtained resin. The water solution of 7.7g (0.19 mols) of sodium hydroxides and 50ml of water was added to this, and it was made to hydrolyze by carrying out heating reflux for 1 hour. Then, 200ml of water was added and diluted, the hydrochloric acid neutralized, and white resin was deposited. This resin was carried out the ** exception, and was rinsed and dried. Furthermore, it dissolved in tetrahydrofuran 200ml, and dropping and reprecipitation were performed, stirring violently in the ultrapure water of 5L. This reprecipitation actuation was repeated 3 times. 120 degrees C of obtained resin were dried in the vacuum desiccator for 12 hours, and the Pori (p-hydroxystyrene / t-butyl methacrylate) copolymer was obtained.

[0225] [Composition of the example of synthetic 3:resin (c-3)] Pori (p-hydroxystyrene) (VP[by Nippon Soda Co., Ltd.]- 8000) 10g was dissolved in pyridine 50ml, and 2 carbonic-acid G t-butyl 3.63g was dropped at this under stirring at the room temperature. After stirring at a room temperature for 3 hours, it was dropped at the solution of ion-exchange-water 1L / 20g of concentrated hydrochloric acid. When the fine particles which deposited were filtered, it rinsed and it dried, the example of resin (c-3) was acquired.

[0226] [Composition of the example of synthetic 4:resin (c-33)] p-cyclohexyl phenol 83.1g (0.5 mols) was dissolved in the toluene of 1 300m, subsequently 2-chloro ethyl-vinyl-ether 150g, 25g [of sodium hydroxides], and tetrabutylammonium bromide 5g and triethylamine 60g were added, and it was made to react at 120 degrees C for 5 hours. Reaction mixture was rinsed, and when superfluous clo ethyl vinyl ether and toluene were distilled off and the obtained oil was refined in vacuum distillation, 4-cyclohexyl phenoxy ethyl vinyl ether was obtained. Pori (p-hydroxystyrene) (VP[by Nippon Soda Co., Ltd.]- 8000) 20g and 4-cyclohexyl phenoxy ethyl-vinyl-ether 6.5g are dissolved in THF80ml, and 0.01g of p-toluenesulfonic acid was added to this, and it was made to react to it at a room temperature for 18 hours. It was dropped agitating reaction mixture violently to distilled water 5L, and when the fine particles which deposit were filtered and it dried, the example of resin (c-33) was acquired.

[0227] It compounded by the same approach using the trunk polymer and vinyl ether to which the example of resin (c-4), (c-28), and (c-30) correspond.

[0228] Pori (P-hydroxystyrene) (VP[by Nippon Soda Co., Ltd.]- 8000) -- instead of -- Pori (P-hydroxystyrene) (VP [by Nippon Soda Co., Ltd.]- 5000) -- using -- being the same -- actuation -- carrying out -- '(c-3) -- '(c-33) -- '(c-4) -- '(c-28) -- '(c-30) -- having obtained . Moreover, the polymer which controlled the amount of an initiator and made molecular weight about 60 percent (the Pori (P-hydroxystyrene / styrene) copolymer (2) and '(c-21) were obtained.)

[0229] (The synthetic example -1 of a lysis-inhibition agent compound: Composition of the example 16 of a compound) 1-[alpha-methyl-alpha-(4'-hydroxyphenyl) ethyl]-4-[alpha' and alpha'-bis(4"-hydroxyphenyl) ethyl] benzene 42.4g (0.10 mols) was dissolved in 300ml of N,N-dimethylacetamide, and 49.5g [of potassium carbonate] (0.35 mols) and bromoacetic acid cumyl ester 84.8g (0.33 mols) was added to this. Then, it agitated at 120 degrees C for 7 hours. After it fed the reaction mixture into 2l. of ion exchange water and the acetic acid neutralized, ethyl acetate extracted. The ethyl-acetate extract was condensed and refined and example of compound 16 (all R is -CH₂ COOC (CH₃)₂ C six H₅ radical) 70g was obtained.

[0230] (The synthetic example -2 of a lysis-inhibition agent compound: Composition of a compound 41) 1, 3, 3, and 5-tetrakis-(4-hydroxyphenyl) pentane 44g was dissolved in 250ml of N,N-dimethylacetamide, and to this, 70.7g of potassium carbonate, subsequently bromoacetic acid t-butyl 90.3g was added, and it agitated at 120 degrees C for 7 hours. The reaction mixture was fed into 2l. of ion exchange water, and the obtained viscous object was rinsed. When the column chromatography refined this, 87g of examples 41 (all R is -CH₂ COOC₄ H₉ (t)) of a compound was acquired.

[0231] (The synthetic example -3 of a lysis-inhibition agent compound: Composition of the example 43 of a compound) alpha -- alpha -- alpha -- ' -- alpha -- ' -- alpha -- " -- alpha -- " - hexa -- kiss (4-hydroxyphenyl) - 1, 3, and 5-triethyl benzene 20g was dissolved in diethylether 400ml. The hydrochloric acid of 3 and 4-dihydro-2H-pyran 42.4g and the amount of catalysts was added to this solution under nitrogen-gas-atmosphere mind, and it flowed back for 24 hours. It filtered, after adding a small amount of sodium hydroxide after reaction termination. When the filtrate was condensed and the column chromatography refined this, 55.3g of examples 43 (all R is a THP radical) of a compound was acquired.

[0232] (The synthetic example -4 of a lysis-inhibition agent compound: Composition of the example 43-2 of a compound) alpha -- alpha -- alpha -- ' -- alpha -- ' -- alpha -- " -- alpha -- " - hexa -- kiss (4-hydroxyphenyl) - it was made to dissolve in 1, 3, and 5-triethyl benzene 20g and 200ml of N,N-dimethylacetamide, and to this, 28.2g of potassium carbonate, subsequently bromoacetic acid butyl 36.0g was added, and it stirred at 120 degrees C for 7 hours. The resultant was fed into 2l. of ion exchange water, and the obtained viscous object was rinsed. When the column chromatography refined this, 37g of said examples 43-2 (all R is -CH₂COOC₄H₉(t)) of a compound was acquired.

[0233] [(a) Synthetic example of the compound which generates a radical (A) directly or indirectly by the exposure of an energy line]

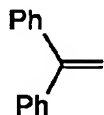
[0234] (Synthetic example -1) 2-bromomethyl -1, 3-dioxolane, and a terephthalic acid -- this -- mol mixture -- potassium carbonate -- 5 time mol -- in addition, it reacted at 60 degrees C. Water was added to mixture and ethyl acetate extracted. after rinsing -- drying (b-6) -- it obtained as a white solid-state. Other compound (b-7) - (b-8) was obtained by same actuation. Moreover, (b-4), - (b-9) (b-40) used the commercial compound.

[0235] A compound (b-4) and - (b-6) (b-40) are as follows.

[0236]

[Formula 90]

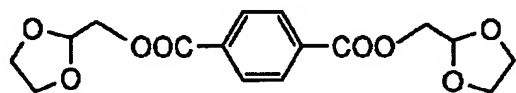
(b-4)



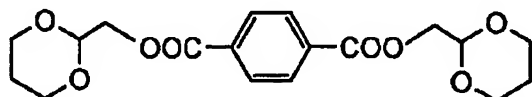
[0237]

[Formula 91]

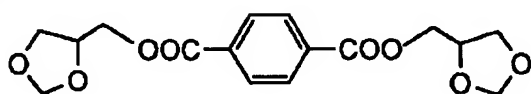
(b-6)



(b-7)

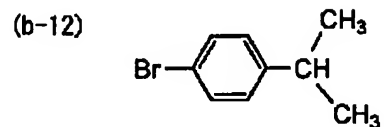
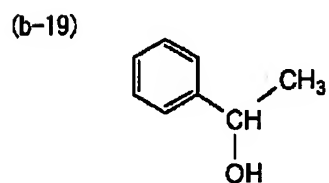
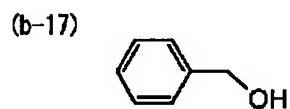
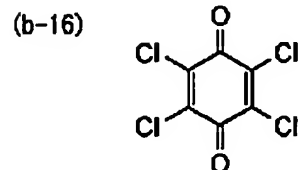


(b-8)



[0238]

[Formula 92]

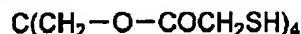
(b-9) CClBr_3 (b-10) CBr_4 (b-11) ICH_2COOH (b-13) $\text{C}_8\text{H}_{17}\text{I}$ (b-14) $\text{C}_8\text{F}_{17}\text{I}$ (b-15) $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{I}$ (b-21) $\text{C}_{18}\text{H}_{37}\text{SH}$ (b-22) $\text{HS}-\text{CH}_2\text{CH}_2\text{COOH}$ (b-24) $\text{HSCH}_2\text{CH}_2\text{OH}$

[0239]
[Formula 93]

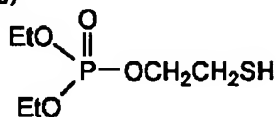
(b-25)



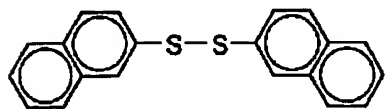
(b-27)



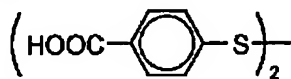
(b-28)



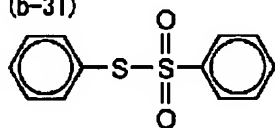
(b-29)



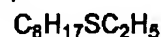
(b-30)



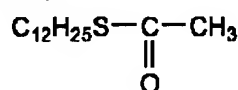
(b-31)



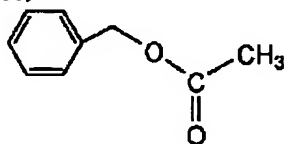
(b-32)



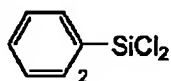
(b-33)



(b-35)



(b-36)



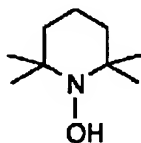
(b-37)



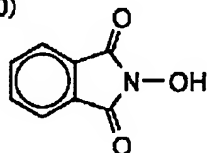
(b-38)



(b-39)



(b-40)



[0240] Example [an example and the example of a comparison]

(1) The component shown in the painting following tables 1-7 of a resist was dissolved in propylene-glycol-monomethyl-ether acetate 8.2g, this was filtered with the 0.1-micrometer Teflon (trademark) filter, and the resist solution was prepared. In addition, 8.2g of ethyl lactates was used for the constituent of an example 35 as a solvent. Each sample solution was applied on the silicon wafer using the spin coater, for 110 degrees C and 90 seconds, it dried with the hot plate of a vacuum adsorption mold, and the resist film A of 0.5 micrometers of thickness was obtained. Furthermore, each sample solution was applied on the silicon wafer using the spin coater, for 110 degrees C and 90 seconds, it dried with the vacuum adsorption mold hot plate, and the resist film B of 0.4 micrometers of thickness was obtained.

[0241] (2) The resist film A and B of ***** of a resist pattern was irradiated by using electron-beam-lithography equipment (pressurization electrical potential difference of 50kV). It heated with the vacuum adsorption mold hot plate after the exposure, respectively (it is 60 seconds (B) at 60 seconds (A) and 110 degrees C in 110 degrees C), and was

immersed for 60 seconds in the tetramethylammonium hydroxide (TMAH) water solution 2.38%, and for 30 seconds, with water, the rinse was carried out and it dried. The cross-section configuration of the obtained contact hole pattern (resist film A use), Rhine, and a tooth-space pattern (resist film B use) was observed with the scanning electron microscope.

[0242] (3) Marginal resolution (the minimum diameter of a hole) in sensibility and the evaluation contact hole pattern of resolution was made into resolution, and the minimum exposure which can resolve the marginal resolution further was made into sensibility. Moreover, the exposure which resolves 0.2 micrometers in a design dimension by 1:1 by Rhine and the tooth-space pattern was made into sensibility, and the resolvable minimum size in this exposure was made into resolution.

[0243] (4) After leaving the resist film obtained by the approach of the evaluation above (1) of PCD for 150 minutes under a high vacuum within electron-beam-lithography equipment, the resist pattern was formed by the approach of (2). It asks for the minimum contact hole size (diameter) or Rhine, and a tooth space resolvable with the same exposure as the sensibility (in this case there being no neglect for bottom 150 minutes of an after [resist film formation] high vacuum immediately exposure) for which it asked by the approach of (3). PCD stability is as good as what shows a value with this near size and marginal resolution acquired by (3).

[0244] (5) When forming the evaluation resist pattern of PED, it carried out by the same approach as (2) except adding the process left for 150 minutes under a high vacuum after an exposure and within electron-beam-lithography equipment. It asks for the minimum contact hole size (diameter) or Rhine, and a tooth space resolvable with the same exposure as the sensibility (in this case, there is no process left for 150 minutes under the high vacuum after an exposure, and it is heated immediately) for which it asked by the approach of (3). PED stability is as good as what shows a value with this near size and marginal resolution acquired by (3).

[0245]

[Table 1]

表1 レジスト膜 A(コンタクトホール)

	酸発生剤	バインダー	(a)の化合物	溶解阻止剤	有機塩基性化合物	界面活性剤*
実施例 1	(II-1) 0.072g	PHS-2 1.19g	b-4 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
2	(II-1) 0.072g	PHS-2 1.19g	b-8 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
3	(II-1) 0.072g	PHS-2 1.19g	b-7 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
4	(II-1) 0.072g	PHS-2 1.19g	b-8 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
5	(II-1) 0.072g	PHS-2 1.19g	b-9 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
6	(II-1) 0.072g	PHS-2 1.19g	b-10 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
7	(II-1) 0.072g	PHS-2 1.19g	b-11 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
8	(II-1) 0.072g	PHS-2 1.19g	b-12 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
9	(II-1) 0.072g	PHS-2 1.19g	b-13 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
10	(II-1) 0.072g	PHS-2 1.19g	b-14 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
11	(II-1) 0.072g	PHS-2 1.19g	b-15 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
12	(II-1) 0.072g	PHS-2 1.19g	b-16 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
13	(II-1) 0.072g	PHS-2 1.19g	b-17 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
14	(II-1) 0.072g	PHS-2 1.19g	b-19 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm

* 対固形分

[0246]

[Table 2]

表2 レジスト膜 A(コンタクトホール)

		酸発生剤	バインダー	(a)の化合物	溶解阻止剤	有機塩基性化合物	界面活性剤*
実施例 15	(II-1)	0.072g	PHS-2 1.19g	b-21 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
16	(II-1)	0.072g	PHS-2 1.19g	b-22 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
17	(II-1)	0.072g	PHS-2 1.19g	b-24 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
18	(II-1)	0.072g	PHS-2 1.19g	b-25 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
19	(II-1)	0.072g	PHS-2 1.19g	b-27 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
20	(II-1)	0.072g	PHS-2 1.19g	b-28 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
21	(II-1)	0.072g	PHS-2 1.19g	b-29 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
22	(II-1)	0.072g	PHS-2 1.19g	b-30 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
23	(II-1)	0.072g	PHS-2 1.18g	b-31 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
24	(II-1)	0.072g	PHS-2 1.19g	b-32 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
25	(II-1)	0.072g	PHS-2 1.19g	b-33 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
26	(II-1)	0.072g	PHS-2 1.19g	b-35 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
27	(II-1)	0.072g	PHS-2 1.19g	b-36 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
28	(II-1)	0.072g	PHS-2 1.19g	b-37 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
29	(II-1)	0.072g	PHS-2 1.19g	b-38 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
30	(II-1)	0.072g	PHS-2 1.19g	b-39 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
31	(II-1)	0.072g	PHS-2 1.19g	b-40 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm

* 対固形分

[0247]

[Table 3]

表3 レジスト膜 A(コンタクトホール)

		酸発生剤	バインダー	(a)の化合物	溶解阻止剤	有機塩基性化合物	界面活性剤*
実施例 32	(II-1)	0.072g	PHS-2 1.19g	b-4 0.18g	(43-2) 0.36g	—	W-1 1000ppm
33	(II-1)	0.072g	PHS-2 1.19g	b-4 0.18g	(43-2) 0.36g	B-1 0.004g	—
34	(II-1)	0.072g	PHS-2 1.19g	b-4 0.18g	(43-2) 0.36g	—	—
35	(II-1)	0.072g	PHS-2 1.19g	b-4 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
36	(II-1)	0.072g	PHS-2 1.19g	b-4 0.18g	(16) 0.36g	B-1 0.004g	W-1 1000ppm
37	(II-1)	0.072g	PHS-2 1.19g	b-4 0.18g	(41) 0.36g	B-1 0.004g	W-1 1000ppm
38	(II-1)	0.072g	PHS-2 1.19g	b-4 0.18g	(43) 0.36g	B-1 0.004g	W-1 1000ppm
39	(II-1)	0.072g	PHS/St2 1.37g	b-4 0.18g	(43) 0.18g	B-1 0.004g	W-1 1000ppm
40	(II-1)	0.072g	(C-3)' 1.37g	b-4 0.18g	(43) 0.18g	B-1 0.004g	W-1 1000ppm
41	(II-1)	0.072g	(C-4)' 1.55g	b-4 0.18g	—	B-1 0.004g	W-1 1000ppm
比較例 1	PAG-1	0.072g	(C-3)' 1.73g	—	—	—	—
2	(I-3)	0.072g	(C-4)' 1.37g	—	(43) 0.36g	—	—

* 対固形分

[0248]

[Table 4]

表4 レジスト膜 A(ラインアンドスペース)

	酸発生剤	バインダー	(a)の化合物	溶解阻止剤	有機塩基性化合物	界面活性剤*
実施例 42	(II-1) 0.072g	PHS-1 1.19g	b-4 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
43	(II-1) 0.072g	PHS-1 1.19g	b-6 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
44	(II-1) 0.072g	PHS-1 1.19g	b-7 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
45	(II-1) 0.072g	PHS-1 1.19g	b-8 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
46	(II-1) 0.072g	PHS-1 1.19g	b-9 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
47	(II-1) 0.072g	PHS-1 1.19g	b-10 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
48	(II-1) 0.072g	PHS-1 1.19g	b-11 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
49	(II-1) 0.072g	PHS-1 1.19g	b-12 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
50	(II-1) 0.072g	PHS-1 1.19g	b-13 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
51	(II-1) 0.072g	PHS-1 1.19g	b-14 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
52	(II-1) 0.072g	PHS-1 1.19g	b-15 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
53	(II-1) 0.072g	PHS-1 1.19g	b-16 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
54	(II-1) 0.072g	PHS-1 1.19g	b-17 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
55	(II-1) 0.072g	PHS-1 1.19g	b-19 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm

* 対固形分

[0249]

[Table 5]

表5 レジスト膜 A(ラインアンドスペース)

	酸発生剤	バインダー	(a)の化合物	溶解阻止剤	有機塩基性化合物	界面活性剤*
実施例 56	(II-1) 0.072g	PHS-1 1.19g	b-21 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
57	(II-1) 0.072g	PHS-1 1.19g	b-22 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
58	(II-1) 0.072g	PHS-1 1.19g	b-24 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
59	(II-1) 0.072g	PHS-1 1.19g	b-25 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
60	(II-1) 0.072g	PHS-1 1.19g	b-27 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
61	(II-1) 0.072g	PHS-1 1.19g	b-28 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
62	(II-1) 0.072g	PHS-1 1.19g	b-29 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
63	(II-1) 0.072g	PHS-1 1.19g	b-30 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
64	(II-1) 0.072g	PHS-1 1.19g	b-31 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
65	(II-1) 0.072g	PHS-1 1.19g	b-32 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
66	(II-1) 0.072g	PHS-1 1.19g	b-33 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
67	(II-1) 0.072g	PHS-1 1.19g	b-35 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
68	(II-1) 0.072g	PHS-1 1.19g	b-36 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
69	(II-1) 0.072g	PHS-1 1.19g	b-37 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
70	(II-1) 0.072g	PHS-1 1.19g	b-38 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
71	(II-1) 0.072g	PHS-1 1.19g	b-39 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
72	(II-1) 0.072g	PHS-1 1.19g	b-40 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
比較例 3	PAG-1 0.072g	(G-3)' 1.73g	—	—	—	—
4	(I-3) 0.072g	(G-4)' 1.37g	—	(43) 0.36g	—	—

* 対固形分

[0250]

[Table 6]

表6 レジスト膜B(ラインアンドスペース)

	酸発生剤	バインダー	(a)の化合物	溶解阻止剤	有機塩基性化合物	界面活性剤*
実施例 73	(II-1) 0.072g	PHS-1 1.19g	b-4 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
74	(II-1) 0.072g	PHS-1 1.19g	b-6 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
75	(II-1) 0.072g	PHS-1 1.19g	b-7 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
76	(II-1) 0.072g	PHS-1 1.19g	b-8 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
77	(II-1) 0.072g	PHS-1 1.19g	b-9 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
78	(II-1) 0.072g	PHS-1 1.19g	b-10 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
79	(II-1) 0.072g	PHS-1 1.19g	b-11 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
80	(II-1) 0.072g	PHS-1 1.19g	b-12 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
81	(II-1) 0.072g	PHS-1 1.19g	b-13 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
82	(II-1) 0.072g	PHS-1 1.19g	b-14 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
83	(II-1) 0.072g	PHS-1 1.19g	b-15 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
84	(II-1) 0.072g	PHS-1 1.19g	b-16 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
85	(II-1) 0.072g	PHS-1 1.19g	b-17 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
86	(II-1) 0.072g	PHS-1 1.19g	b-19 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm

* 対固形分

[0251]

[Table 7]

表7 レジスト膜B(ラインアンドスペース)

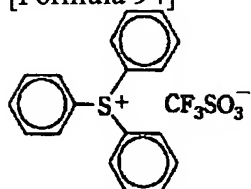
	酸発生剤	バインダー	(a)の化合物	溶解阻止剤	有機塩基性化合物	界面活性剤*
実施例 87	(II-1) 0.072g	PHS-1 1.19g	b-21 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
88	(II-1) 0.072g	PHS-1 1.19g	b-22 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
89	(II-1) 0.072g	PHS-1 1.19g	b-24 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
90	(II-1) 0.072g	PHS-1 1.19g	b-25 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
91	(II-1) 0.072g	PHS-1 1.19g	b-27 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
92	(II-1) 0.072g	PHS-1 1.19g	b-28 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
93	(II-1) 0.072g	PHS-1 1.19g	b-29 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
94	(II-1) 0.072g	PHS-1 1.19g	b-30 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
95	(II-1) 0.072g	PHS-1 1.19g	b-31 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
96	(II-1) 0.072g	PHS-1 1.19g	b-32 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
97	(II-1) 0.072g	PHS-1 1.19g	b-33 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
98	(II-1) 0.072g	PHS-1 1.19g	b-35 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
99	(II-1) 0.072g	PHS-1 1.19g	b-36 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
100	(II-1) 0.072g	PHS-1 1.19g	b-37 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
101	(II-1) 0.072g	PHS-1 1.19g	b-38 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
102	(II-1) 0.072g	PHS-1 1.19g	b-39 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
103	(II-1) 0.072g	PHS-1 1.19g	b-40 0.18g	(43-2) 0.36g	B-1 0.004g	W-1 1000ppm
比較例 5	PAG-1 0.072g	(G-3)' 1.73g	—	—	—	—
6	(I-3) 0.072g	(G-4)' 1.37g	—	(43) 0.36g	—	—

* 対固形分

[0252] Acid generator PAG-1 is as follows.

[0253]

[Formula 94]



PAG-1

[0254] The presentation of the used binder resin, the physical properties, etc. are as follows.

(c-3): p-HITOROKISHI styrene / p-t-butoxy carboxy styrene copolymer (mole ratio: 80/20), weight average molecular weight (Mw) 13000, molecular-weight-distribution (Mw/Mn) 1.4(c-3)':Mw8000 [0255] (c-4): p-hydroxystyrene / p-(1-ethoxy ethoxy) styrene copolymer (mole ratio: 70/30), Mw12000, molecular-weight-distribution (Mw/Mn) 1.3(c-4)':Mw7000 [0256] (c-21): p-hydroxystyrene / t-butyl methacrylate copolymer (mole ratio: 70/30), Mw16000, molecular-weight-distribution (Mw/Mn) 2.0(c-21)':Mw9500 [0257] (c-22): p-hydroxystyrene / p-(1-t-butoxyethoxy) styrene copolymer (mole ratio: 85/15), Mw12000, molecular-weight-distribution (Mw/Mn) 1.1(c-22)':Mw7000 [0258] (c-28): p-hydroxystyrene / p-(1-phenethyl oxyethoxy) styrene copolymer (mole ratio: 85/15), Mw12000, molecular-weight-distribution (Mw/Mn) 1.2(c-28)':Mw7000 [0259] (c-30): p-hydroxystyrene / p-(1-phenoxy ethoxy ethoxy) styrene copolymer (mole ratio: 85/15), Mw13000, molecular-weight-distribution (Mw/Mn) 1.2(c-30)':Mw8000 [0260] (c-33): p-hydroxystyrene / p-(1-p-cyclohexyl phenoxy ethoxy) styrene copolymer (mole ratio: 85/15), Mw13000, molecular-weight-distribution (Mw/Mn) 1.2(c-33)':Mw8000 [0261] : (PHS-1) Pori (P-hydroxystyrene) (the Nippon Soda Co., Ltd. make, trade name VP-8000)

: (PHS-2) Pori (P-hydroxystyrene) (the Nippon Soda Co., Ltd. make, trade name VP-5000)

: (PHS-3) Pori (P-hydroxystyrene) (the Toho Chemical Co., Ltd. make, trade name H-80A)

: (PHS-4) Pori (P-hydroxystyrene) (the Toho Chemical Co., Ltd. make, trade name H-60A)

[0262] (PHS/St: What was compounded in the synthetic example 1) :p-hydroxystyrene / styrene (mole ratio: 80/20), Mw26000, molecular-weight-distribution (Mw/Mn) 1.9(PHS/St2):Mw15600 [0263] About an organic base nature compound, it is as follows.

B-1: 2, 4, 5-triphenyl imidazole B-2:1, 5-diazabicyclo [4.3.0] nona-5-en B-3:4-dimethylamino pyridine B-4:1, and 8-diazabicyclo [5.4.0] undeca-7-en B- 5:N-cyclohexyl-N'-morpholino ethyl thiourea [0264] About a surfactant, it is as follows.

W-1: Troysol S-366 (made in Troy Chemical)

W-2: Megger fuck F176 (Dainippon Ink make)

W-3: Megger fuck R08 (Dainippon Ink make)

W-4: Polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make)

W-5: Sir chlorofluorocarbon S-382 (Asahi Glass Co., Ltd. make)

[0265]

[Table 8]

表8 レジスト膜 A(コンタクトホール)

	感度 ($\mu\text{C}/\text{cm}^2$)	解像力 (μm)	プロファイル	PCD (μm)	PED (μm)
実施例 1	0.8	0.06	矩形	0.08	0.06
2	2.1	0.05	矩形	0.05	0.05
3	1.4	0.06	矩形	0.06	0.06
4	2.2	0.09	矩形	0.09	0.09
5	0.8	0.08	矩形	0.08	0.08
6	2.0	0.09	矩形	0.09	0.09
7	1.7	0.09	矩形	0.08	0.09
8	1.6	0.08	矩形	0.08	0.08
9	0.9	0.09	矩形	0.09	0.09
10	2.0	0.09	矩形	0.09	0.09
11	1.1	0.10	矩形	0.10	0.10
12	2.2	0.06	矩形	0.08	0.06
13	2.2	0.08	矩形	0.08	0.08
14	1.5	0.09	矩形	0.09	0.09

[0266]

[Table 9]

表9 レジスト膜 A(コンタクトホール)

	感度 ($\mu\text{C}/\text{cm}^2$)	解像力 (μm)	プロファイル	PCD (μm)	PED (μm)
実施例 15	1.4	0.08	矩形	0.08	0.08
16	1.4	0.07	矩形	0.07	0.07
17	2.4	0.08	矩形	0.08	0.08
18	2.2	0.09	矩形	0.09	0.09
19	0.8	0.05	矩形	0.05	0.05
20	1.0	0.07	矩形	0.07	0.07
21	1.1	0.10	矩形	0.10	0.10
22	0.7	0.05	矩形	0.05	0.05
23	0.8	0.07	矩形	0.07	0.07
24	1.1	0.10	矩形	0.10	0.10
25	1.0	0.05	矩形	0.05	0.05
26	1.4	0.06	矩形	0.06	0.06
27	1.7	0.07	矩形	0.07	0.07
28	1.2	0.05	矩形	0.05	0.05
29	2.4	0.10	矩形	0.10	0.10
30	0.7	0.07	矩形	0.07	0.07
31	0.8	0.09	矩形	0.09	0.09

[0267]

[Table 10]

表 10 レジスト膜 A(コンタクトホール)

	感度 ($\mu\text{C}/\text{cm}^2$)	解像力 (μm)	プロファイル	PCD (μm)	PED (μm)
実施例 32	0.6	0.09	矩形	0.10	0.10
33	1.5	0.11	矩形	0.11	0.11
34	0.6	0.12	矩形	0.13	0.13
35	1.2	0.11	矩形	0.11	0.11
36	1.5	0.06	矩形	0.06	0.06
37	1.2	0.07	矩形	0.07	0.07
38	1.8	0.08	矩形	0.08	0.08
39	1.5	0.07	矩形	0.07	0.07
40	1.2	0.06	矩形	0.08	0.08
41	1.1	0.09	矩形	0.09	0.09
比較例 1	7.0	0.17	キャッピング、底状	0.25	0.23
2	5.5	0.18	キャッピング、底状	0.28	0.25

[0268]

[Table 11]

表 11 レジスト膜 A(ラインアンドスペース)

	感度($\mu\text{C}/\text{cm}^2$)	解像力(μm)	プロファイル	PCD(μm)	PED(μm)
実施例 42	0.6	0.05	矩形	0.05	0.05
43	1.7	0.04	矩形	0.04	0.04
44	1.1	0.05	矩形	0.05	0.05
45	1.8	0.08	矩形	0.08	0.08
46	0.6	0.07	矩形	0.07	0.07
47	1.6	0.08	矩形	0.08	0.08
48	1.4	0.08	矩形	0.08	0.08
49	1.3	0.07	矩形	0.07	0.07
50	0.7	0.08	矩形	0.08	0.08
51	1.6	0.08	矩形	0.08	0.08
52	0.9	0.09	矩形	0.09	0.09
53	1.8	0.05	矩形	0.05	0.05
54	1.8	0.07	矩形	0.07	0.07
55	1.2	0.08	矩形	0.08	0.08

[0269]

[Table 12]

表 12 レジスト膜 A(ラインアンドスペース)

	感度($\mu\text{C}/\text{cm}^2$)	解像力(μm)	プロファイル	PCD(μm)	PED(μm)
実施例 56	1.1	0.07	矩形	0.07	0.07
57	1.1	0.06	矩形	0.06	0.06
58	1.9	0.07	矩形	0.07	0.07
59	1.8	0.08	矩形	0.08	0.08
60	0.6	0.04	矩形	0.04	0.04
61	0.8	0.06	矩形	0.06	0.06
62	0.9	0.09	矩形	0.09	0.09
63	0.6	0.04	矩形	0.04	0.04
64	0.6	0.06	矩形	0.06	0.06
65	0.8	0.09	矩形	0.09	0.09
66	0.8	0.04	矩形	0.04	0.04
67	1.1	0.05	矩形	0.05	0.05
68	1.4	0.08	矩形	0.06	0.06
69	1.0	0.04	矩形	0.04	0.04
70	1.9	0.09	矩形	0.09	0.09
71	0.8	0.06	矩形	0.08	0.06
72	0.6	0.08	矩形	0.08	0.08
比較例 3	7.1	0.15	テーパー形状	0.23	0.20
4	5.6	0.14	テーパー形状	0.24	0.23

[0270]

[Table 13]

表 13 レジスト膜B(ラインアンドスペース)

	感度($\mu\text{C}/\text{cm}^2$)	解像力(μm)	プロファイル	PCD(μm)	PED(μm)
実施例 73	0.8	0.06	矩形	0.08	0.06
74	2.1	0.05	矩形	0.05	0.05
75	1.4	0.06	矩形	0.06	0.06
76	2.2	0.09	矩形	0.09	0.09
77	0.8	0.08	矩形	0.08	0.08
78	2.0	0.09	矩形	0.09	0.09
79	1.7	0.09	矩形	0.09	0.09
80	1.6	0.08	矩形	0.08	0.08
81	0.9	0.09	矩形	0.09	0.09
82	2.0	0.09	矩形	0.09	0.09
83	1.1	0.10	矩形	0.10	0.10
84	2.2	0.06	矩形	0.06	0.06
85	2.2	0.08	矩形	0.08	0.08
86	1.5	0.09	矩形	0.09	0.09

[0271]

[Table 14]

表 14 レジスト膜 A(コンタクトホール)

	感度($\mu\text{C}/\text{cm}^2$)	解像力(μm)	プロファイル	PCD(μm)	PED(μm)
実施例 87	1.4	0.08	矩形	0.08	0.08
88	1.4	0.07	矩形	0.07	0.07
89	2.4	0.08	矩形	0.08	0.08
90	2.2	0.09	矩形	0.09	0.09
91	0.8	0.05	矩形	0.05	0.05
92	1.0	0.07	矩形	0.07	0.07
93	1.1	0.10	矩形	0.10	0.10
94	0.7	0.05	矩形	0.05	0.05
95	0.8	0.07	矩形	0.07	0.07
96	1.1	0.10	矩形	0.10	0.10
97	1.0	0.05	矩形	0.05	0.05
98	1.4	0.06	矩形	0.06	0.06
99	1.7	0.07	矩形	0.07	0.07
100	1.2	0.05	矩形	0.05	0.05
101	2.4	0.10	矩形	0.10	0.10
102	0.7	0.07	矩形	0.07	0.07
103	0.8	0.09	矩形	0.09	0.09
比較例 5	7.1	0.15	テーパー形状	0.24	0.21
6	5.6	0.15	テーパー形状	0.24	0.23

[0272] The positive-resist constituents of this invention are high sensitivity and high resolution, a rectangle pattern profile is given and the result of Tables 8-14 shows that PCD and PED stability are extremely excellent further.

[0273] In examples 1, 4, 5, 14, 15, 20, 21, 29, 30, and 31, when the organic base nature compound was changed into B-2, B-3, B-4, and B-5 from B-1, respectively and was carried out, the equivalent engine performance was obtained.

Moreover, in examples 1, 4, 5, 14, 15, 20, 21, 29, 30, and 31, when the surfactant was changed into W-2, W-3, W-4, and W-5, respectively and was carried out from W-1, the equivalent engine performance was obtained.

[0274] In examples 1, 4, 6, 8, 13, and 14, when PHS-2 were changed into PHS-4 and they were carried out similarly, the equivalent engine performance was obtained. an example -- 41 -- setting -- a binder -- respectively (c-21) -- ' -- ' (c-22) -- ' (c-28) -- ' (c-30) -- ' (c-33) -- changing -- having carried out -- a place -- being equivalent -- the engine performance -- obtaining -- having had . Moreover, in the example, when PHS-1 was changed into PHS-3 and it was carried out similarly, the equivalent engine performance was obtained.

[0275] In examples 1, 4, 5, 14, 15, 20, 39, 40, and 41, when the solvent was changed into propylene-glycol-monomethyl-ether acetate / propylene-glycol-monomethyl-ether =80 / 20 (weight ratio) and was carried out similarly, the same effectiveness was acquired.

[0276] In examples 1, 5, 11, and 28, when the acid generator was changed into (I-7), (I-8), (I-9), and (II-3), respectively (I-1) and was carried out, the equivalent engine performance was obtained.

[0277] Moreover, the component of a publication was dissolved in the above-mentioned solvent, moreover, the above-mentioned table 1 was reached account example 1-31, the constituent liquid of 35 was filtered with the 0.1-micrometer filter made from polyethylene, and the resist solution was prepared. About each of these resist solutions, the homogeneity within a field was evaluated as follows.

[0278] (Homogeneity within a field) Each resist solution was applied on the 8 inch silicon wafer; the same processing as painting of the above resist layers was performed, and the resist spreading film for the homogeneity measurement within a field was obtained. In LambdaA by the great Japan screen company, 36 of these were equally measured so that it might become a cross joint along the wafer diameter direction about spreading thickness. The standard deviation of each measured value was taken and O and 50 or more things were evaluated for that with which the 3 times do not fill 50 as x. Consequently, the homogeneity within a field of the thing (examples 1-31) using propylene-glycol-monomethyl-ether acetate (PGMEA) as a resist spreading solvent was O. The homogeneity within a field of the thing (example 35) using ethyl lactate (EL) as a resist spreading solvent to it was x. Therefore, in this invention, it turns out that it is desirable to use PGMEA as a resist spreading solvent.

[0279] (6) The resist film of 0.40 micrometers of thickness was obtained by the same approach as the resist film B of the above (1), using respectively each resist constituent of the patterning above-mentioned example 42 and the examples 1 and 2 of a comparison by actual size X-ray lithography. Subsequently, except having used the actual size X-ray aligner (gap value; 20nm), patterning was performed like the above (2) and the same approach as the above (3) estimated the resist engine performance (sensibility, resolution, and pattern configuration). An evaluation result is shown in Table 15.

[0280]

Table 15 resist constituent Sensibility (mJ/cm²) Resolution (micrometer) Pattern configuration Example 42 50 0.10

Rectangle Example 1 of a comparison 185 0.18 A taper configuration, ***** Example 2 of a comparison 185 0.18

Taper configuration [0281] It turns out that the engine performance in which the resist constituent of this invention was extremely excellent also in X-ray lithography is shown so that more clearly than the above-mentioned table 15. [0282]

[Effect of the Invention] The positive type chemistry magnification resist constituents of this invention are high sensitivity and high resolution, they can give the pattern profile which was excellent in the shape of a rectangle, and, moreover, the stability and spreading nature of PCDPED are extremely excellent.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law

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[Procedure amendment 1]

[Document to be Amended] Specification

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[Method of Amendment] Modification

[The contents of amendment]

[Claim(s)]

[Claim 1] (a) The compound which generates a radical (A) directly or indirectly by the exposure of an energy line
The positive type chemistry magnification resist constituent characterized by containing.

[Claim 2] (b) The compound which generates an acid by the exposure of an energy line

The positive type chemistry magnification resist constituent according to claim 1 characterized by containing.

[Claim 3] (e) It is insoluble in the resin to which it has the radical which may be decomposed with an acid and the solubility over an alkali developer increases according to an operation of an acid, or (g) water, and is resin meltable to an alkali developer.

The positive type chemistry magnification resist constituent according to claim 1 or 2 characterized by containing.

[Claim 4] (f) The with a molecular weight of 3000 or less low-molecular lysis inhibition compound to which it has the

radical which may be decomposed with an acid and the solubility over an alkali developer increases according to an operation of an acid

The positive type chemistry magnification resist constituent according to claim 1 to 3 characterized by containing.

[Claim 5] This radical (A) reacts with the compound (a) which generates an acid by the exposure of the (a) energy line, and an acid is generated.

The positive type chemistry magnification resist constituent according to claim 1 to 4 by which it is characterized.

[Claim 6] The positive type chemistry magnification resist constituent according to claim 1 to 5 characterized by the thing for which this compound (a) is chosen from the following group, and which is a kind at least.

(1) Alkyl halides other than a fluorine,

Aryl halides other than a fluorine,

Halogenation aralkyls other than a fluorine,

Allyl halides other than a fluorine

It is (however, as for the above-mentioned alkyl, aryl, an aralkyl, and an allyl group, a part or all hydrogen may be permuted by the fluorine),

(2) Thiol compounds, the second class alcohol, the allyl alcohol that may have a substituent, the benzyl alcohol which may have a substituent on a ring and these ester, an ether compound

A sulfide compound, a disulfide compound

(3) A halogen-containing silicon compound, an alkoxy silicon compound

(4) The shape of a straight chain, the letter of branching, or an annular acetal compound

(5) N-hydroxyl compound

[Claim 7] The pattern formation approach which forms the resist film with a positive type chemistry magnification resist constituent according to claim 1 to 6, irradiates an energy line at the resist film concerned, and is characterized by developing negatives.

[Translation done.]